Edible Films from Starch and Chitosan:

Formulation and Gas Permeabilities

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Starch and chitosan films are both known to be effective barriers to gas permeation. Being naturally abundant, renewable, and biodegradable, starch and chitosan films have the potential to replace petroleum-based materials for food packaging applications. However, the gas permeability of starch-chitosan blend films has not been studied extensively. In order to characterize starch-chitosan blend films for food packaging application, the permeabilities of N_2, O_2 and CO_2 in the blend films were studied at different operating conditions (e.g., relative humidity, chitosan content in the films, cross membrane pressure, and temperature).

The gas permeation was measured using the traditional volumetric technique. Gas permeation through films containing different amounts of chitosan was measured at ambient temperature and at a cross membrane pressure of 60psi. In addition, pure chitosan was also tested at a high relative humidity where the gas was saturated with water vapor. The effects of temperature and cross membrane pressure on the gas permeability were studied with starch-chitosan blend films and pure chitosan films as well. It was found that an increase in pressure and/or temperature increased the permeability, and the temperature dependence of permeability followed the Arrhenius relation, from which activation energy of permeation was evaluated. The starch-chitosan blend films with approximately 60wt% chitosan showed the best gas barrier property and the highest activation energy for permeation.

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I am especially thankful for what the Lord has given to me. His guidance and his love made me learn and grow. May the Heavenly Father continue to guide me in my life.

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Chapter 1

Introduction

1.1 Background

Skin and shells are the natural protection for fruits and nuts. The natural barriers control the permeation of gases such as oxygen, carbon dioxide, and moisture and as well reduce fungal contamination [Miller and Krochta, 1997]. The purpose of packaging is to preserve freshness of the content inside the barrier to maintain and prolong the quality throughout the product's shelf-life and thus increase the shelf-life [Miller and Krochata, 1997; Pareta and Edirisinghe, 2006].

Petroleum-based food packaging has been widely used. However, environmental concerns about petroleum pollutions and oil scarcity call for finding alternative substitutions [Jansson *et al.,* 2006]. Over the past decade, a significant amount of research has been invested in edible and biodegradable films from natural polymers including cellulose, starch, and chitosan because they are naturally abundant, biodegradable and made from renewable sources [Jansson *et al.,* 2006; Miller and Krochta, 1997]. These films have the potential to replace conventional packaging in some applications. Although they have high water vapor permeability, starch and chitosan are known to be effective barrier to gas transport. Starch and chitosan can be potential candidates since they are not only biodegradable and edible but also widely available, easy to handle and inexpensive [Bertuzzi *et al.,* 2007; Rdríguez *et al.,* 2006; Rindlav-Westling *et al.,* 1998]. In order to utilize starch and chitosan film for food

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packaging applications to extend shelf-life, it's important to regulate the gas and water vapor transport across the film [Bertuzzi *et al.,* 2007; Rankin *et al.,* 1958]. The desired film must permeate CO_2 for the respiration of fruits and vegetables and minimal amount of O_2 for products containing fat to avoid spoilage [Rankin *et al.,* 1958]. Starch contains linear polymers of amylose and branched polymers of amylopectin. The starch film property changes with amylose to amylopectin ratio, type of plasticizers used, plasticizer content, and relative humidity. Chitosan is derived from chitin which can be found from shellfish. Chitosan film property also varies with operating conditions including relative humidity, temperature, and cross membrane pressure. Since starch and chitosan films have the potential to replace conventional food packaging, characterization of the film and possibility of improving the film by mixing the two should be investigated. There has been some research on the mechanical property and water vapor permeability on starch and chitosan blend films but very little on the gas permeation properties.

1.2 Research objectives

Since starch and chitosan have the potential to be used as an alternative food packaging material, it is necessary to characterize their permeability of gases that are present in air, namely N_2, O_2 and CO_2. Furthermore, since the gas barrier properties of starch and chitosan films are greatly affected by operating conditions, the relationships between gas barrier properties and the film composition (i.e., starch to chitosan ratio), cross membrane pressure, and temperature are investigated. The objectives of this research are the following:

- Formulate and select a suitable membrane formation method and procedure for starch, chitosan and starch-chitosan films

- Investigate the effect of chitosan concentration in starch-chitosan blend films on the gas permeability of the films in order to achieve a low O_2 permeability and a high CO_2 permeability

- Evaluate the effect of cross membrane pressure on the gas permeability of starch-chitosan blend films

- Examine the effect of temperature on the gas permeability of starch-chitosan films

1.3 Thesis outline

In this thesis, an introduction of the background knowledge, the objectives and the outline of the research are presented in Chapter 1. More comprehensive literature background and review of the materials (starch and chitosan) and the film property are shown in Chapter 2. Comparisons of the mechanical and gas barrier properties on different types of starch and chitosan films under different operating conditions are also presented in Chapter 2. A comparison of the gas permeability reported in literature is shown in Appendix A. Chapter 3 outlines the experimental procedures of membrane preparation and measurements. The experimental results are discussed in Chapter 4 (with the raw data presented in Appendixes B, C and D). The gas permeabilities of N_2, O_2, and CO_2 through starch-chitosan blend films are tested at different of chitosan contents in the film, cross membrane pressures, and temperatures. Lastly, Chapter 5 concludes the thesis with recommendations for future work.

Chapter 2

Literature Review

2.1 Transport Mechanism

2.1.1 Theory and background

Membrane is a "discrete and thin interface" that regulates the permeation [Baker, 2004]. The primary use of a membrane is based on its ability to control the permeation rates of different chemical species through the membrane and therefore separate two or more components. Membranes are used in many processes including the well-developed processes of microfiltration, ultrafiltration, reverse osmosis and electrodialysis and the developing processes of gas separation and pervaporation [Baker, 2004]. Gas permeability through membranes has been systematically studied since Graham measured the permeation rate of all the gases and diaphragm films available in late 1800s [Graham, 1867].

Membranes can be categorized as symmetrical and anisotropical. There are two types of symmetrical membranes, porous and dense membranes. Depending on the pore size, different transport mechanisms take place, for example, diffusion versus molecular sieving. Generally, if the pore size is smaller than 5Å [Baker, 2004], the membrane can be characterized as dense which separates two species by concentration gradient; if the pore size is larger than 10 Å, the membrane is considered to be porous and species are separated by

molecular size. If the pore size is between 5 – 10 Å, the membrane separates species by both concentration gradient and molecular size [Baker, 2004]. The transport of gas molecules in a dense membrane consists of 3 steps: sorption of the permeant onto the membrane surface, diffusion of the permeant from one side of the membrane to the other side, and then the desorption of the permeant from the membrane, as shown in Figure 2.1.
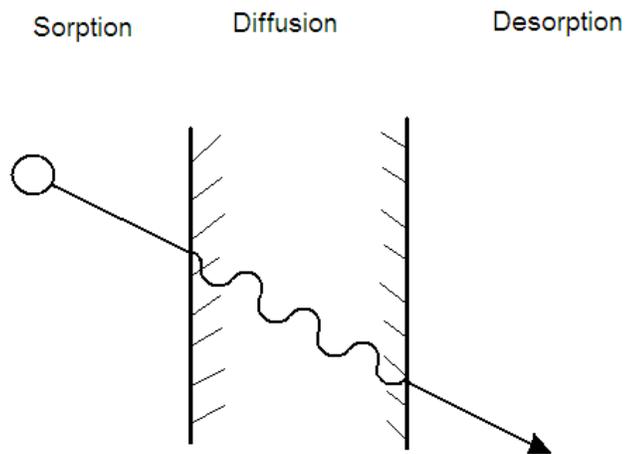
Figure 2.1 Solution-diffusion mechanism for mass transport in a dense membrane

In the following, the theories of solution-diffusion for gas permeation and separation using dense membranes will be discussed.

Diffusion is a process where chemical species transports to the other side of membrane under a concentration gradient. The Fick's first law can be used to describe diffusion at steady state:

$$J = -D\frac{dC}{dx} \tag{2.1}$$

where J is the diffusion flux, D is diffusion coefficient or diffusivity, and C is the concentration of a gas in the membrane. Integration of equation 2.1 with respect to concentration over the membrane thickness, the following equation is obtained:

$$J = D\frac{C_1 - C_2}{l}$$ (2.2)

where C_1 and C_2 are the concentrations of the gas on the feed and permeate sides of the membrane, respectively, and l is the thickness of the membrane. From Henry's law of solubility, the concentration of the gas can be expressed as:

$$C = Sp$$ (2.3)

where S is the solubility coefficient of the gas in the membrane, and p is the pressure of the gas. Combining equation 2.2 and 2.3 gives the following equation:

$$J = DS\frac{p_1 - p_2}{l}$$ (2.4)

The product of diffusion coefficient and solubility coefficient is equal to the permeability coefficient, which characterizes the intrinsic permeability of the membrane,

$$P = DS$$ (2.5)

In this thesis, "permeability" will be used interchangeably with "permeability coefficient" P defined in equation 2.5. The selectivity of the membrane to the permeation of a pair of gases can be measured by their permeability ratio, which will be discussed in more details later.

2.2 Starch

2.2.1 Starch: source, structure, property and manufacture

Starch is a naturally occurring polymer which is inexpensive and abundantly available. It is the main storage of carbohydrate in most plants and is also widely consumed polysaccharide in the human diet [Yuryev *et al.,* 2002]. There are many types of starches and the most common types are corn, tapioca, potato, wheat and rice starch. Among these types, potato has the largest granules and rice starch has the smallest [Gregorová *et al.,* 2006]. Most starches are not uniform and contain two types of complex carbohydrate polymers of glucose: a linear chain polymer termed amylose (Figure 2.2) and a branched polymer of glucose termed amylopectin (Figure 2.3) [Gregorová *et al.,* 2006; Rdríguez *et al.,* 2006; Zobel and Stephen, 2006].
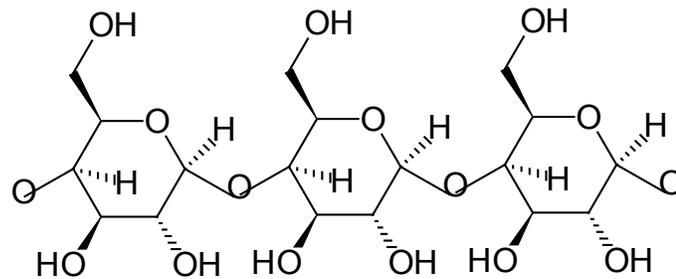
Amylose

Figure 2.2 Amylose Structure
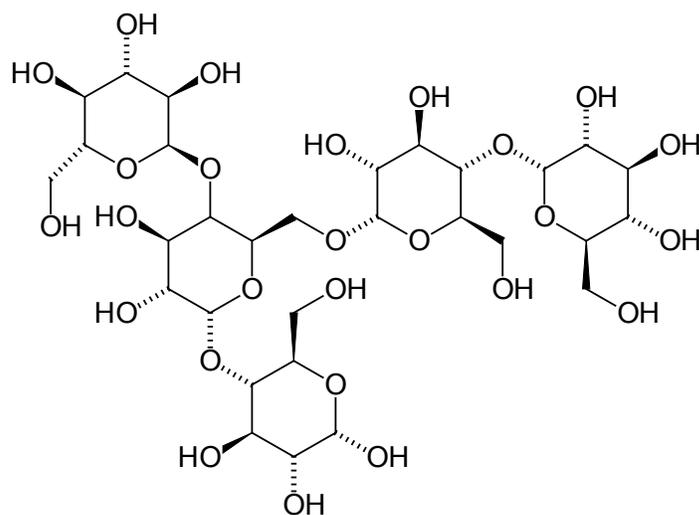
Amylopectin

Figure 2.3 Amylopectin Structure

The amylose to amylopectin ratio in a starch differs from types of starches and therefore they show different properties. The amylose to amylopectin ratios for different types of starches are shown in Table 2.1. When heated, starch granules swell and amylose will leach into the aqueous phase. Afterward, it undergoes gelatinization when cooled. Starch gelatinization occurs at different temperatures depending on the type of starch. Generally, the gelatinization completes at around 70° C under atmospheric pressure [Zobel and Stephen, 2006]. The gelatinization temperature increases with the addition of glycerol and decreases with the addition of alkali salt [Takahashi and Wada, 1992].

Table 2.1. Amylose contents in starches

Starch Source	Amylose (%)	Reference
Waxy Corn	0	Xu *et al.*, 2005
Tapioca	17	Zobel and Stephen, 2006
Rice	17	Zhu *et al.*, 2007
Potato	21	Daniel and Whisler, 1993
Wheat	25	Hung *et al.*, 2006
Corn	27	Vasques *et al.*, 2007

Corn starch is manufactured from corn directly. After harvesting, corn is cleaned prior to steeping. During the steeping process, corn is soaked in hot water in order to break the starch and protein bonds. Depending on the type of starch being manufactured, water, temperature, time and agitation, are crucial to good starch cooking [Askew, 2003; Kearney, 2004]. At this stage, the gluten bonds, a type of protein bonds, in the corn begin to release starch [Askew, 2003]. After the steeping process, the germ separation begins. Because water is added to assist the wet milling, the surface water should be removed at the germ drying step by a screw press and then fed to rotary steam tube bundle dryers. Oil is also extracted from the germ. The corn oil can be used for other food applications such as cooking oil or margarine. The typical yield of corn oil is about 27kg per ton of corn [Askew, 2003]. After the extraction, the fiber will be ground, screened and then dried. Further, gluten will be recovered from the starch milk, followed by many steps of drying and refinery to produce starch powder [Askew, 2003].

2.2.2 Non-food starch applications

Papermaking is the largest non-food application for starch, either modified or unmodified. Other non-food starch applications include pharmaceutical, adhesive, textile, detergent, paint, surfactant, mining and building industries [Blennow *et al.,* 2003; Glenn *et al.,* 2007; Kittipongpatana *et al.,* 2006]. The paper industry consumes about 5 million tons starch globally and 1.36 million tons in North America annually [Kearney, 2004; Mishra, 2005]. The amount of starch used in papermaking depends on the type of paper being made; when the paper is primarily made from fiber, starch is used for conveying and enhancing [Mishra, 2005]. In addition, starch foam is also a new potential application for starch to replace the traditional plastic foam made from polystyrene, polyurethane, and poly(vinyl chloride) [Fang and Hanna, 2001].

2.3 Applications of Starch Film for food packaging

Because of the rising need of replacing petroleum based plastics for food packaging, much effort has been invested into the research of starch film. Starch film is known to have good barrier properties and a high water vapor permeability [Bertuzzi *et al.,* 2007]. Starch film is brittle and therefore plasticizer is often used to make the film more flexible. By adding a plasticizer, the film flexibility increases at the cost of lower barrier properties. The challenge of using starch film for food packaging is the balance between the gas barrier and mechanical properties [Glenn *et al.,* 2007]. Many researchers have studied the barrier properties of starch films, including the effects of plasticizers and water content, temperature,

and relative humidity. The following sections will discuss about the effects of different parameters on the properties of starch films.

2.3.1 Effect of plasticizer content

2.3.1.1 Water vapor permeability

Plasticizers are used in starch film formulations in order to overcome problems associated with brittleness. Plasticizers reduce the intermolecular forces and increase the chain mobility, thereby increasing the flexibility and water or gas diffusion of the films [Guilbert S., 1986; Koskinen M. *et al.,* 1996]. Plasticizers can also decrease the glass transition temperature below ambient temperature [Lourdin D. *et al.* 1997]. The common plasticizers used are glycerol, sorbitol, sodium lactic acid, ethylene glycol, and PEG 200. Generally, water vapor permeability increases with an increase in the plasticizer content [Talji, *et al.*, 2007]. Rindlav-Westling *et al.*[1998] performed water vapor permeability measurements on plasticized (40wt% glycerol) amylose and amylopectin films (from potato) at relative humidity 50%. It was observed that amylopectin films had a higher water vapor permeability (12.56 g/m.day.atm) than that of amylose films (10.44 g/m.day.atm). Bertuzzi *et al.* [2007] investigated the effect of glycerol content (0-60wt%) on the water vapor permeability of high amylose (70%) starch films and found that the water vapor permeability increased linearly with an increase in the glycerol content and the water vapor permeability at 60wt% glycerol was at least twice as large as the water vapor permeability in glycerol free films.

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Talja *et al.* [2007] compared the water vapor permeability of starch films with different plasticizers: glycerol, xylitol, and sorbitol. The films with sorbitol as the plasticizer had the lowest water vapor permeability, while the films with glycerol were the highest. At a given plasticizer content, the lower the relative humidity gradient, the larger the difference in water vapor permeability of the films with different types of plasticizers [Talja *et al.*, 2007]. Moreover, the increase in water vapor permeability is less significant at lower relative humidity but similar relative humidity gradients [Müller *et al.*, 2008].

Thirathumthavorn and Charoenrein [2007] investigated on the water vapor permeability of tapioca films plasticized with sorbitol over a storage time of 2 months. The water vapor permeabilities of the starch films were 2.68, 2.75, and 3.28 g/m.day.atm at a storage time of 0, 1 and 2 months, respectively. It is evident that the water vapor permeability was not significantly affected by the storage time.

2.3.1.2 Gas permeability

Because the permeability coefficient as an approximation is the product of solubility coefficient and diffusivity coefficient (Equation 2.5), the diffusivity is enhanced by the addition of plasticizers. Thus, the permeability normally also increases with the plasticizer content. Gaudin *et al.* [2000] measured the oxygen permeability of starch films with sorbitol (8.8-28 wt%) and found that the permeability with 28wt% sorbitol was 3.5 to 718 times larger than that with 8.8wt% sorbitol at a relative humidity of 57- 90%. It was concluded that the higher the relative humidity, the larger the effect of plasticizer on oxygen permeability

[Gaudin *et al.*, 2000]. This is consistent with the water vapor permeability observations mentioned earlier.

Forssell *et al.* [2002] investigated on the effect of glycerol contents (0-30wt%) on the oxygen permeability of amylose and amylopectin films at 20°C. It was reported that the permeability of amylopectin film increased with an increase in the plasticizer content above 10wt% at a relative humidity of 50%, while the permeability of amylose film was independent of the plasticizer content at a relative humidity 50%. However, amylopectin films with 20wt% glycerol was shown to have a lower oxygen permeability than the films containing 10wt% glycerol at a relative humidity of 90%, while the oxygen permeability increased with an increase in glycerol contents in amylose films at relative humidity 90% [Forssell *et al.,* 2002]. It was found that without glycerol, amylopectin films were better barriers, and amylose films were less permeable to oxygen if they contained over 15wt% of glycerol. It was also reported that the plasticized films are more permeable to oxygen at a higher water content [Forssell *et al.*, 2002].

Dole *et al.* [2004] also reported that starch films from potato have good barrier properties at low plasticizer levels in comparison with ethylene and vinylic alcohol copolymer membranes. Since the permeability is directly related to the diffusivity, Dole *et al.* studied on the effects of water and plasticizer contents (12-25 wt%). It was found that the increased oxygen permeability with increasing plasticizer was in agreement with Forssell *et al.* [2002]. The oxygen permeabilities of starch films with a glycerol content of 12, 18 and 25wt% are 0.002, 0.005, and 0.014 barrer, respectively, at a relative humidity of 50%. Good

barrier properties are shown to be independent of the plasticizer content for the range tested. It was also observed that the permeability coefficient varies exponentially with the glycerol content in the range of 12-40 wt%, and the gas permeability is roughly constant when the plasticizer content is less than 10 wt%.

2.3.1.3 Mechanical properties

The main reason for adding plasticizers to starch films is to improve the mechanical properties of the films. Without plasticizers, the films are rigid and brittle; when the plasticizer content is above 40 wt%, the films are sticky even at a low relative humidity [Talja *et al.*, 2007]. The tensile properties of plasticized amylose and amylopectin films at relative humidity of 50% were studied by Rindlav-Westling *et al.* [1998] and the amylose films were found to be stronger than amylopectin films. Laohakunjit and Noomhorm [2004] researched on the relationship between the plasticizer content (glycerol and sorbitol) and the tensile strength of rice starch. It was found that the films with sorbitol had a higher tensile strength than films with glycerol. The tensile strength of the films without plasticizer is 9MPa and it is decreased by the addition of plasticizers. With 35 wt% glycerol, Talja *et al.* [2007] reported that the rice starch film had a tensile strength as low as 1 MPa. On the other hand, Talja *et al.* [2007] investigated the effects of types of plasticizers (glycerol, xylitol, and sorbitol) and plasticizer content (20 to 60wt%) on the tensile strength of potato starch. At all the relative humidity tested (33, 54 and 76%), the starch film with 20wt% glycerol showed the highest tensile strength, and the films with 40wt% glycerol showed the lowest. In general, the higher the plasticizer content, the lower the tensile strength.

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2.3.1.4 Antiplasticizing

The addition of a plasticizer usually increases the intermolecular forces and therefore overcomes the film brittleness problem and increase the gas permeability and water vapor permeability most of the time. However, antiplasticizing effect has also been observed. The term 'antiplasticizing' is used when the addition of a plasticizer shows a decrease in the film permeability. Gaudin *et al.* [2000] found that the water uptake and oxygen permeability in wheat starch films were the lowest at 21wt% sorbitol content in the range of sorbitol content (0-28wt%) tested. The oxygen permeability through the starch film at 8.8wt% sorbitol is comparable to the permeability of ethylene vinyl alcohol polymer (EVOH) (20 and 16 barrers, respectively) [Gaudin *et al.,* 2000]. It was believed that the interaction between starch and sorbitol caused a decrease in oxygen diffusion.

Most water-compatible plasticizers were reported to have plastizicing effects [Chang *et al.*, 2006]; this may be due to the limited range of plasticizer concentrations studied. It was also mentioned that only Lourdin *et al.* [1997] earlier provided experimental data suggesting that glycerol might have an antiplasticizing effect on glassy potato starch film, although a certain small amount of glycerol also showed the usual plasticizer effect

2.3.2 Water content

The effect of water content on the permeability of hydrophilic films is important. Forssell *et al.* [2002] researched on the effects of water content (relative humidity 50 - 90%) on amylose, amylopectin and synthetic films at 20℃. When the relative humidity is below 50%, the starch films crack [Forssell *et al.*, 2002]. The amylose films have a very low oxygen

permeability at room temperature when they are dry. At ambient relative humidity, both starch and synthetic films were good oxygen barriers; above relative humidity 70%, the oxygen permeability in starch films increased dramatically. At a relative humidity of 90%, the permeabilities of amylose and amylopectin films were both significantly higher than that of the synthetic films. The behavior of amylose and amylopectin films was similar; under ambient humidity, the oxygen barrier of starch film is as good as Ethylene Vinyl Alcohol Polymer. The increase in permeability with water content is likely due to the increase in polymer chain mobility, facilitating the transport at a higher water content [Forssell *et al.,* 2002].

It was also reported by Dole *et al.* [2004] that starch films have a low gas permeability if the hydration level is low. Low gas permeability indicates good gas barrier properties which is in agreement with Forssell *et al.* [2002] relative humidity below 65%. Gaudin *et al.* [2000] measured the oxygen permeabilities of starch films plasticized with sorbitol at a high relative humidity (57-90%), and it was observed that the oxygen permeability increased exponentially with an increase in relative humidity when the relative humidity is over 70%. The water vapor permeability was also affected by the relative humidity; the relative humidity gradient was not the only dominating factor but if one side has a high relative humidity, the water vapor permeability is much higher [Müller *et al.*, 2008; Talja *et al.*, 2007].

2.3.3 Temperature and water effects

The diffusivity and solubility coefficients of a permeant are dependent on temperature. Since permeability coefficient is the product of diffusivity and solubility coefficients, temperature also affects the gas permeability. An increase in temperature usually causes a small decrease in solubility and an increase in diffusion of water vapor [Bertuzzi *et al.,* 2007]; therefore, the permeability tends to increase with an increase in temperature. Generally, the temperature dependence on water vapor permeability follows the Arrhenius expression [Bertuzzi *et al.*, 2007]. The activation energy of permeation in plasticized high amylose starch film (70% amylose) was 5.61 kJ/mol, which was higher than the activation energy of permeation in cellophane (1.67 kJ/mol) but lower than the activation energy of permeation in hydroxypropyl cellulose (14.56kJ/mol) and methyl cellulose (16.43kJ/mol) [Bertuzzi *et al.*, 2007]. For comparison, the activation energies for water vapor permeation in polypropylene and polyethylene are 42.2-65.3 and 33.4-61.7 kJ/mol, respectively, and they are much higher than the activation energy of water vapor permeation in starch films.

2.3.4 Effect of amylose content

Rindlav-Westling *et al.* [1998] researched the barrier properties of amylose and amylopectin films from potato. At low glycerol content, amylopectin films had a lower oxygen permeability, while at a higher glycerol content, amylose films were less permeable than amylose films. They also observed a high oxygen permeability in amylopectin film at

40wt% glycerol where the oxygen permeability in amylopectin is about twice as much as in amylose. Mali *et al.* [2006] researched on the films under controlled storage (64% relative humidity and 20˚C) by measuring glass transition temperature, crystallinity, mechanical property, and water vapor permeability in cassava (19% amylose), corn (25% amylose), and yam (29% amylose) starches. It was found that the yam starch film had the lowest glass transition temperature, the highest degree of crystallinity, the highest tensile stress (both initial sample and stored sample), and the lowest water vapor permeability at a low glycerol content. The films with a higher amylose content were shown to have better characteristics for being food packaging films.

2.4 Chitosan

Chitin is a naturally occurring polysaccharide found in the exoskeleton of crabs, shrimps, and lobsters. It is the second most abundant polysaccharide next to cellulose [Arvanitoyannis *et al.,* 1998; No *et al.,* 2007; Xu *et al.,* 2005]. Chitosan is derived from chitin, which is manufactured 2000 metric tons annually [Sandford, 2003].
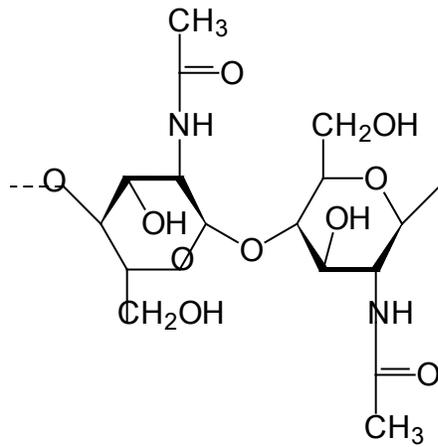
Chitin

Figure 2.4 Chitin Structure
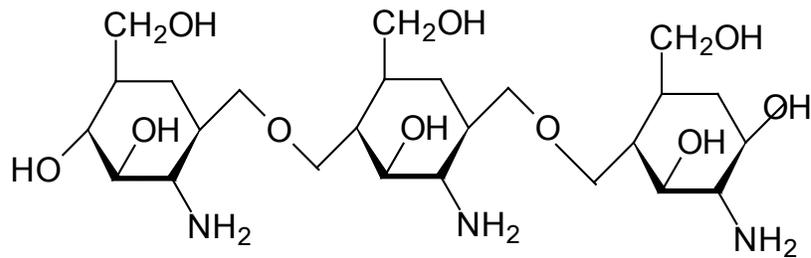
Chitosan

Figure 2.5 Chitosan Structure

2.4.1 Chitosan source, structure, property, manufacture and applications

Chitin and chitosan are manufactured from crustacean. The dissolution of calcium carbonate and removal of protein are the main steps in the manufacture [Dutta *et al.,* 2002].

Crustacean shells are first demineralized with HCl in order to remove calcium and CO_2 followed by washing with NaOH in order to remove proteins [Vårum and Smidsrød, 2006]. Chitin and chitosan are known to have properties of flocculation, film forming [Butler *et al.,* 1996], gelation [Vorlop and Klein, 1981], antimicrobial [Vårum and Smidsrød, 2006], emulsification [Knorr 1982], and dye binding [Knorr 1983].

The possible applications of chitin and chitosan include edible films, additive, antimicrobial agents, and in purification of water. An example of chitosan as flocculant would be to remove humic acid from drinking water [Vårum and Smidsrød, 2006; Eikebrokk, 1999]. Other applications of chitosan as flocculant are removal of suspended solid, metal, toxic chemicals, and dyes [Vårum and Smidsrød, 2006].

2.5 Applications of Chitosan Film for Food Packaging

Chitosan has the unique properties of hydrophilicity and basic property due to its amino and hydroxyl groups. Chitosan may be preferred to permeate acidic gas such as CO_2 [Ito *et al.*, 1997]. Also because of its antimicrobial activity, many studies have been done on its uses in food such as meat, seafood, fruit, and sausage [Ho *et al.¸* 2007]. Sathivel *et al.* [2007] measured water vapor permeability and permeabilities of N_2, O_2 and CO_2 gases through a chitosan film at 35% relative humidity, 25°C and at a cross-membrane pressure of 29 psi. The water vapor permeability, and the permeabilities of N_2, O_2 and CO_2 were 2.56 g/m.day.atm and 0.046, 0.081, and 0.259, barrer, respectively, and the CO_2/O_2 selectivity was 3.1. The water vapor permeability value was similar to the value reported by Park [1999] (4.29 g/m.day.atm). Other researchers have also tried to measure O_2 permeability on chitosan

films, and it was found to be 0.48 barrer by Wang *et al.* [1992] and 16.78 barrer by Muzzarelli *et al.* [1974]. The testing conditions were not specified and therefore the results are not expected to be the same but it may indicate that the gas permeability is influenced by the relative humidity, cross-membrane pressure or other parameters involved.

2.5.1 Effect of water content

Just like starch, chitosan is also hydrophilic, and its permeability is greatly affected by water content in the membrane. It was shown in literature that by feeding water vapor-containing gases, the gas permeability increased. Ito *et al.*, [1996] tested the permeability of N_2 and CO_2 at different relative humidities and obtained a selectivity of 29. When mixed gases of N_2 and CO_2 were allowed to permeate through a chitosan film at room temperature, a selectivity of 70 was reported. Liu *et al.*[2008] measured the gas permeability in water-swollen hydrogel membranes including poly(vinyl alcohol), chitosan, carboxyl methyl cellulose, alginic acid and poly(vinylamine). It was observed that these hydrophilic films have low permeability at dry states but the permeability increases significantly with an increase in water content in the membrane. Bae *et al.* [1998] found that N_2 and CO_2 in wet chitosan membranes are 11-15 and 15-17 times more permeable than the in dry chitosan membrane.

Despond *et al.* [2001] did a more coherent investigation on the effect of relative humidity on gas permeability. O_2 and CO_2 permeabilities were measured at 20°C and at different relative humidities ranging from 0 to 100%. It was found that O_2 and CO_2

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permeabilities increased by 12.9 and 172.7 times, respectively, when the relative humidity increased from 0 to 100% and the corresponding selectivity of CO_2/O_2 increased from 1.25 to 16.71. Ito *et al.* [1997] also noticed that when chitosan membrane is wet, the permeabilities and selectivities tend to be higher.

2.5.2 Effect of temperature

El-azzami and Grulke [2007] investigated the effect of temperature on gas permeabilities of a dry chitosan membrane to CO_2, H_2, and N_2 in their gas mixtures. The temperature range tested was 20-150°C with a feed pressure of 1.5 atm. The CO_2 permeability was shown to increase from 0.381 to 26.1 barrers with a CO_2/N_2 selectivity decreasing from 19.7 to 4.55 [El-azzami and Grulke, 2007]. The decreasing selectivity with increasing temperature showed that temperature has a greater effect on N_2 permeation. The activation energy of permeation of N_2 and CO_2 are 44.9 and 24.1 kJ/mol, respectively.

Liu *et al.* [2008] measured the permeabilities of N_2, He, H_2, and CO_2 in water-swollen chitosan membranes at temperatures from 23 to 60°C. The gas permeability was also shown to increase with an increase in temperature. These results are similar to those obtained with dry chitosan membranes [El-azzami and Grulke, 2007]. The activation energy of permeation, which is lower for the water-swollen chitosan membrane than to dry chitosan obtained by El-azzami and Grulk [2007], is 21.3 and 6.58 kJ/mol for N_2 and CO_2, respectively.

2.5.3 Other effects

Caner *et al.* [1998] reported the effects of types of acids and concentration used in film formation and storage time on the gas permeability and mechanical properties of chitosan films. Among the acids used for preparing chitosan solutions (acetic, formic, lactic, and propionic acids), chitosan films prepared using acetic acid showed the lowest water vapor permeability, and the chitosan films prepared using formic acid showed the highest. However, water vapor permeability was not very sensitive to the types of acids used as the measured water vapor permeability ranged from 0.83 to 1.057 g/m.day.atm. Moreover, the oxygen permeability is the lowest when lactic acid was used in preparing the film, while the films prepared using formic acid has the highest permeability to oxygen. Chitosan films prepared using acetic acid showed the second lowest oxygen permeability and the lowest water vapor permeability. This may be why acetic acid was used in chitosan film preparation in many studies [Caner *et al.,* 1998]. During a 9 week storage time investigated, the oxygen permeability, water vapor permeability, and tensile strength were shown to remain the same.

2.5.4 Examples of applications

Chitosan coating are known to increase the storability and decrease fungal activities for fruits since the early 90s. It was also reported that chitosan-coated (1wt%) strawberries were preserved better than Rovral®-treated (liquid fungicide) ones as they were firmer and had less infected berries after a certain period of storage time [Ghaouth *et al.,* 1991]. The

antimicrobial and film-forming properties of chitosan make it a good candidate for food coating/packaging material [No *et al.,* 2007].

Chitosan coating on baguette has been investigated by Park *et al.* [2002]. It was found that baguette coated with 1wt% chitosan showed less weight loss and the shelf-life was extended by 24 hours when comparing the treated baguette at 36 hours and control at 12 hours [Park *et al.,* 2002]. Ahn *et al.* [2003] also reported that mould was detected in the control after 4 days but was not detected in the chitosan treated bread after 8 days.

2.6 Starch and chitosan blend films

Since both starch and chitosan are biodegradable and suitable for food packaging applications, the possibility of improving the barrier and mechanical properties of the films by combining the two has gained much attention but not yet studied extensively. Homogeneous, transparent, and flexible films can be obtained from corn starch and chitosan [Garcia *et al.,* 2006]. They reported the opacity, film solubility, and water vapor permeability of the starch-chitosan blend films. Opacity is described as the amount of radiation that is blocked by the object which is important in food surface coating [Garcia *et al.*, 2006]. The films were conditioned at 20℃ and 65% relative humidity before measurements. The opacity increased with starch concentration and decreased with glycerol content. The solubility measurement of the films was done at room and boiling temperatures by agitation in water for over 7 days. It was found that the film solubility increased with the addition of glycerol due to its hydrophilicity [Garcia *et al.*, 2006]. The blend of starch and chitosan has a higher

film solubility (15.5%) than either starch (13.48%) or chitosan (8.6%) [Garcia *et al.*, 2006]. It is also found that the film solubility only increased by approximately 10% when the temperature increased from 25 to 100°C, indicating that solubility was not greatly affected by water temperature.

Plasticized corn starch and chitosan blend films were found to have a lower water vapor permeability than the single component films [Garcia *et al.*, 2006]. Addition of plasticizer (i.e., glycerol) can greatly reduce (by~30%) the water vapor permeability of starch films according to data from Garcia *et al.* [2006], while plasticized blend films have a slightly lower water vapor permeability than pure chitosan film.

Xu *et al.* [2005] investigated the effects of types of starch used, namely regular corn starch (25% amylose) and waxy starch (0% amylose), and the ratio of starch to chitosan on the mechanical properties and water vapor permeation rate [Xu *et al.*, 2005]. It was shown that the water vapor permeation rate was the highest when chitosan concentration was 67wt%, and the waxy starch had a higher permeation rate than regular starch. Pure chitosan film had a water vapor permeation rate of 52.73 g/m^2h whereas at 33wt% chitosan, the water vapor permeation rate was lower for both waxy and regular starches. Xu *et al.* [2005] measured the mechanical properties of the films from regular corn starch , waxy starch, and chitosan films, all conditioned at 50% relative humidity. It was reported that the tensile strength increased with the addition of starch (either type) and decreased when the starch to chitosan ratio is over 1:1. Blend films of chitosan and regular starch had a higher tensile strength (40.25 MPa at 50wt% chitosan) than blend films with waxy starch (33.68 MPa at

50wt% chitosan) [Xu *et al.*, 2005]. This is in a good agreement with results from Mathew *et al.* [2006] who obtained a maximum tensile strength is 37.5MPa at 40wt% chitosan using potato starch. This value is comparable with those obtained (43-45 MPa) with regular corn starch and 20wt% chitosan from Zhai *et al.*, [2004]. As explained by the researchers, the increase in tensile strength from 100 to 50wt% chitosan content is due to the formation of inter-molecular hydrogen bonds between starch (OH$^-$) and chitosan (NH$_3^+$). The further decrease in tensile strength with the addition of starch in films after 50wt% chitosan may be due to the formation of intra-molecular hydrogen bonds in starch [Xu *et al.*, 2005]. Moreover, because amylose is a linear polymer, it is more easily associated with chitosan molecules which are also linear.

It was also shown that the higher the chitosan content (in the range of 0 - 20wt%), the lower the optical density of antibacterial activity of *E Coli.*[Zhai *et al.*, 2004]. The results indicated that the pure starch showed little or no improvement compared to control (without irradiation), whereas the film with 20wt% chitosan showed 60% improvement in the optical density.

Previous studies showed that starch and chitosan blend films have a higher tensile strength and lower water vapor permeation rate than films from either individual component alone. On the other hand, there are also some drawbacks of the blend film such as a higher relative solubility in water.

2.7 Other similar experiments

Similar to chitosan, water-soluble chitin was added to amylose film [Suzuki *et al.*, 2005]. The gas permeabilities of N_2, O_2 and CO_2, measured at 25˚C and room humidity, were observed to increase dramatically when water-soluble chitin was added. The increase was much less intense after water-soluble chitin concentration reached around 20wt%. The gas permeability increased by at least 2 times when water-soluble chitin increased from 0 to around 15wt% [Suzuki *et al.*, 2005]. These phenomena indicated that the addition of water-soluble chitin to amylose film did not show a simple addition property of the two and thus they were miscible. It was also shown that the elongation of the blend film is stronger than films of either component alone. The tensile strength also increased when water-soluble chitin was added and reached a plateau at around 5wt% water-soluble chitin. The highest tensile strength was around 50MPa, which was higher than tensile strength of starch film (~10MPa) and chitosan film (~45MPa) [Talja *et al.*, 2007; Suzuki *et al.*, 2005; Xu *et al.*, 2005; Zhai *et al.*, 2004]. The antibacterial effect also increased dramatically when water-soluble chitin was added. Pure amylose film and water-soluble chitin film had more than 6 million CFU (colony forming unit), while the blend films had less than half a million CFU. This behavior of the blend (such as tensile strength, or water vapor permeation rate) as compared to the single component films is similar to the starch-chitosan blend film [Xu *et al.*, 2005].

Arvanitoyannis *et al.* [1998] prepared edible films with chitosan and gelatin. Gelatin was made from pigskin and it has a melting point close to body temperature. Films were

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formed in a manner similar to the starch-chitosan films with plastizicers (glycerol, sorbitol and sucrose). It was shown that the blends have lower melting and transition temperatures as the plasticizer contents increases [Arvanitoyannis *et al.,* 1998]. They also showed that when the plasticizer content increases, both water vapor permeability and elongation increase, while the tensile strength and modulus decrease for all the plasticizers tested at both high-temperature (60°C) and low-temperature (22°C) [Arvanitoyannis *et al.,* 1998]. It was observed that the increase in water vapor permeability is directly proportional to the increase in total plasticizer content. The gas permeability increased with an increase in the plasticizer content, which agrees with the results from starch-chitosan blend films.

Chillo *et al.* [2008] studied on the influence of glycerol and chitosan on tapioca starch films using surface response curve. It was found that the higher the chitosan concentration (up to 1wt% tested), and the lower the glycerol (0.5 to 1.2wt% tested), the higher the tensile strength. This is similar to the results of Talja *et al.* [2007] with rice starch films.

Durango *et al.* [2006] evaluated the antimicrobial effect against *S. enteritidis* on yam starch and chitosan. The data showed that the pure starch had the lowest antimicrobial effect and pure chitosan had the highest. The blends of yam starch and chitosan showed very similar antimicrobial effect at two different concentrations of chitosan (33 and 50wt%)

Mathew and Abraham [2008] further studied ferulic acid incorporated starch-chitosan blend films. Ferulic acid was oxidized by hydrogen peroxide and then added to the starch-chitosan blend with 25wt% glycerol as plasticizer. The blend films were then dried at 50°C and 50% relative humidity. A large increase in the tensile strength was observed (62.71 MPa

with 0.075wt% ferulic acid) as compared to blend films obtained without ferulic acid (~45 MPa) [Mathew and Abraham, 2008; Xu *et al.,* 2005; Zhai *et al.*, 2004]. The increase in tensile strength could be due to the formation of the cross linkage introduced by ferulic acid. The water vapor permeability decreased slightly when oxidized ferulic acid was added, while the addition of oxidized ferulic acid increased the tensile strength of the film greatly.

Many other studies about adding a coating layer to the starch-chitosan films or the similar are also carried out, including beewax [Gällstedt and Hedenqvist, 2002], carrageenan [Ribeiro *et al.*, 2007], and methylcellulose and soybean oil [Bravin *et al.*, 2006] in order to reduce the water vapor permeability and oxygen permeability. A comparison of the gas permeability through the various starch and chitosan films is summarized in Appendix A. The present study focuses on the formulation and gas barrier properties of edible films from starch and chitosan in order to get an insight into the relationship between the gas permeability and the film composition as well as the effects of temperature and cross-membrane pressure.

Chapter 3

Experimental

3.1 Materials

The films used in this study were made from starch and chitosan. Regular corn starch was chosen because of its low cost and availability. Moreover, it has been shown that amylose films have a higher tensile strength and a lower water vapor permeability than amylopectin films [Rindlav-Westling *et al*., 1998]. Corn starch has a higher amylose content than rice, tapioca, and potato starches. Therefore, corn starch is likely to have superior film property. Corn starch (27% amylose) was supplied from Sigma. Chitosan flakes (MW ~100,000) was purchased from Kyowa Technos Co (Japan). The plastizicer used for this research was glycerol (99.9wt%) provided by Baker. Glacial acetic acid from Fischer Scientific was used to dissolve chitosan flakes. Non-woven fabric was used as the support for all the membranes made in this research.

3.2 Membrane Preparation

Aqueous solutions of starch were obtained by dispersing corn starch (5wt%) in de-ionized water. The detailed procedure is as the follows: A predetermined amount of starch was mixed with water in a container with air tight lid it and was placed on a stirring/heating plate. A stir bar was used for mixing, and the heating was maintained at approximately

5ºC/min until the solution reached 85 ºC. During the heating process, the lid was opened a few times to allow the excess vapor to escape in order to prevent pressure build-up inside the container. Glycerol (20 wt% of starch) was then added into the solution. The solution was kept at 85 ºC for 30 min to ensure complete gelatinization.

The temperature 85ºC was chosen in the heating process because the viscosity of starch solution increases dramatically at around 70ºC, and the viscosity continued to increase as a result of swelling up to a maximum of 212.5mPa s at 82.8 ºC [Vasques $et. al.,$ 2007]. After this point, the viscosity decreases due to the breakdown of the starch granules. In order to prevent excessively losing water content during the solution preparation, the solution was covered with a lid at all times. The solution was finally cooled at room temperature to 55ºC while still under agitation.

Chitosan solution was prepared by dissolving 1wt% chitosan flakes in 2wt% acetic acid. Acetic acid was chosen because the resulting chitosan films have a lower oxygen and water vapor permeability [Caner $et al.,$ 1998]. It takes ~3 days to dissolve completely under stirring at room temperature, and un-dissolved residual solids were removed by filtration. For the case of a pure chitosan film, after the chitosan solution was obtained, it was cast directly. For the case of starch-chitosan blend films, the chitosan solution was mixed with gelatinized starch solution at 55ºC until a homogenous blend was obtained before film casting.

All the films were cast onto a non-woven fabric as support. It was found during the experiment that without a support, the film is more fragile. With non-woven fabric as support, thin films can be formed which are sufficiently strong during permeability test under

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pressure. In addition, after being placed in the permeation cell, the membrane swelling due to the humidified gas will not deform the membrane. Attempt was made to obtain films with similar thicknesses (~25µm). The membranes were dried inside a fume hood at ambient conditions for 48 h, and they were then cut to desired sizes. For conditioned films, they were stored in a humidifier for at least 24 h before permeation measurements. All the films were conditioned (pre-humidified) prior to measurements except for the data in 4.1.1 in order to examine the effect of relative humidity on gas permeation.

3.3 Permeation tests

A schematic diagram of the permeation measurement setup is shown in Figure 3.1. The membrane sample with an effective permeation area of 16.6cm^2 was mounted into the permeation cell. Pure gas (N_2, O_2 or CO_2, research grade) at a given pressure flowed through a water vapor saturator before admission to the permeation cell. The feed gas pressure varied from 20 to 100 psig, while the permeate side was under atmospheric pressure. Humidified gas was used to prevent the membrane from drying during gas permeation measurement. The permeation rate was measured with a bubble flowmeter. The membranes were tested at different operating conditions (cross membrane pressures and temperatures) During the startup of each test with a different gas, the feed side was purged with the feed gas at a low pressure (~5psig) to ensure the feed side of the permeation cell was free from residual gas from previous measurement. The feed pressure was then adjusted to the desired values. About 3 h of stabilization was needed before measurement of steady state permeation rate.
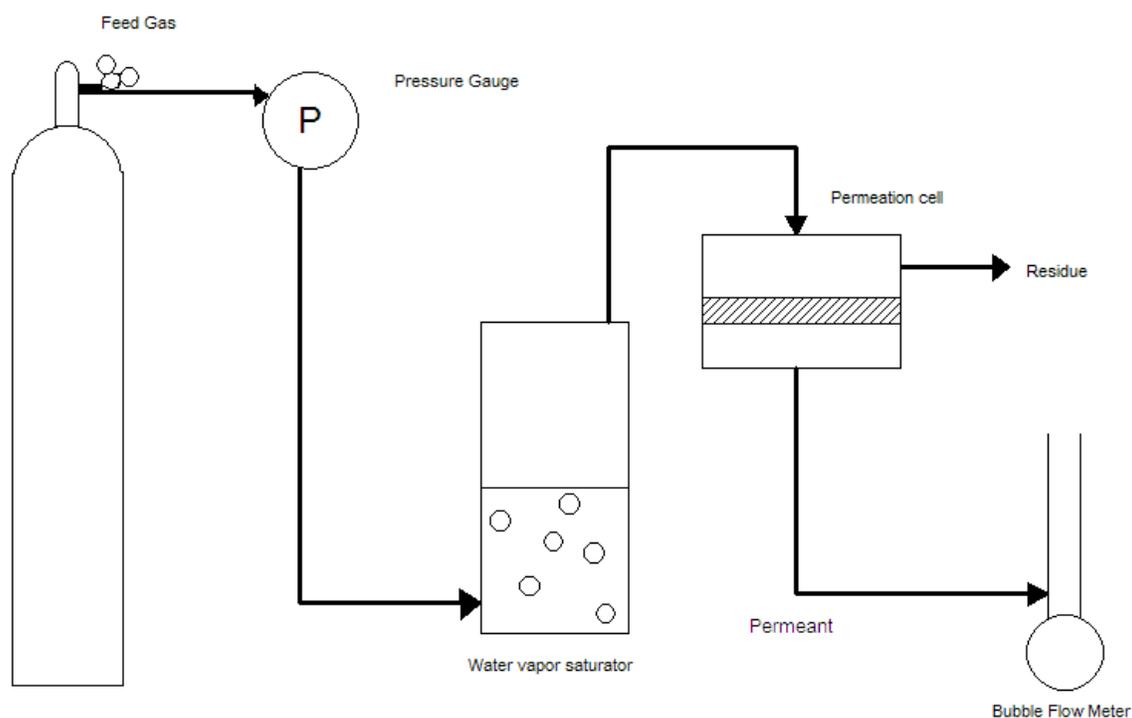
Figure 3.1 schematic of gas measurement set-up

Chitosan content in the blend films is an important parameter. To evaluate the effect of film composition on the membrane permeability, the permeation measurements were performed at 60psig and at room temperature (24 °C). The permeability of starch-chitosan blend and pure chitosan films were tested at different cross membrane pressures (20, 40, 60, 80, and 100 psi) and at room temperature. Between measurements at different pressures, 1 h of stabilization was allowed. When varying the temperature, the water vapor saturator and the permeation cell were immersed in a water bath. The temperatures tested were: 20, 25, 30, 35, and 40 °C. Because the gas for permeation is inside the saturator and permeation cell,

more time (1.5 h) was allowed to stabilize the membrane conditions between changing

temperatures.

3.4 Calculations

The permeation rate was measured with a bubble flow. The permeability coefficient

was calculated from:

$$P = \frac{Q}{S \cdot t \cdot \Delta p} l \qquad (3.1)$$

where Q is the quantity of permeant collected [cm^3 (STP)], S is the effective membrane area

for permeation [cm^2], t is the time required to collect the permeant [s], Δp is the pressure

difference across the membrane [cmHg], and l is the thickness of the membrane [cm]. The

permeability coefficient has the unit of [cm^3(STP).cm/(cm^2.s.cmHg)] which can be converted

into barrer [10^{-10} cm^3(STP).cm/(cm^2.s.cmHg)]. The thickness used in the calculation is the

thickness of the starch-chitosan films excluding the thickness of the microporous non-woven

fabric support.

Selectivity is defined as the ratio of permeability of gas A to the permeability of gas B

where gas A is more permeable:

$$\alpha_{A/B} = \frac{P_A}{P_B} \qquad (3.2)$$

The temperature dependence of permeability usually follows the Arrhenius relation:

$$P = P_o \exp(\frac{-E_P}{RT})$$

(3.3)

where P is the permeability coefficient, T is the temperature, Ep is the activation energy of permeation [kJ/mol], R is gas constant, and P_o is pre-exponential factor.

Chapter 4
Results and Discussion

As discussed earlier, the use of starch and chitosan blend films as food packaging material has many advantages over either single component films alone, but their characterization was not studied extensively. Since the food packaging material will be exposed to air, the gas barrier property of N_2, O_2, and CO_2 through the film needs to be characterized. There are some studies on O_2 permeability in starch films, and on N_2, O_2, and CO_2 permeability in chitosan films, as well as water vapor permeability and mechanical properties of starch-chitosan blend films. To the best of my knowledge, the present study is the first on N_2, O_2 and CO_2 permeabilities in starch-chitosan blend film. In this study, gas permeation through starch-chitosan blend films was evaluated for films with different chitosan contents, at different cross membrane pressures and temperatures.

The experimental data are presented in Appendixes B-D. It was shown that for all the conditions tested, N_2 had the lowest permeability and CO_2 had the highest. This is in agreement with literature data on chitosan and chitosan-gelatin blend films [Arvanitoyannis *et al.*, 1998; Sathivel *et al.*, 2007]. As mentioned earlier, the permeability coefficient equals the product of diffusivity and solubility coefficients. The molecular size and shape directly affect how fast the molecule diffuses from one side of the membrane to the other side. The kinetic diameter can be used to represent the effective dimension of a molecule by its size

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and shape. If the electron cloud around a nucleus is more compact, the kinetic diameter of the molecule is smaller. For the three gases studied here, their kinetic diameters are in the order of $CO_2 > O_2 > N_2$ (see Table 4.1). The kinetic diameter of CO_2 is not much larger than that of O_2 and N_2, but CO_2 is much more permeable than the other gases because of its much higher solubility in moist films due to presence of water in the films, as shown in Table 4.1.

Table 4.1 Solubility, diffusivity, and kinetic diameter data on N_2, O_2 and CO_2 in water at 25°C [Lide, 2007-7008; Lin *et al.*, 2004; Salamone J.C., 1996;]

Gas	Solubility Parameter (cm^3(STP)/(cm^3.cmHg))	Diffusivity (cm^2/s)	Kinetic Diameter (Å)
N_2	1.94×10^{-4}	2.00×10^{-5}	3.64
O_2	3.75×10^{-4}	2.42×10^{-5}	3.46
CO_2	1.01×10^{-2}	1.91×10^{-5}	3.30

Generally, the more easily condensed gas is the more soluble in polymer. CO_2 is more condensable than O_2 and N_2 and it has a much higher solubility than O_2 and N_2. On the other hand, the solubility and diffusivity of O_2 are larger than N_2. This characteristics attributes to the permeability in the order of $CO_2 > O_2 > N_2$.

Ito *et al.* [1997] speculates that the basic property of chitosan may favor the permeation of acidic gases such as CO_2. Acetic acid was used in the process of making chitosan films. After the membrane is dried, there is little acetic acid left in the film and the basic property of chitosan is in effect. The high solubility of CO_2 in water and the acid-base interaction between CO_2-chitosan make CO_2 a more preferentially permeable.

4.1 Effect of Chitosan Content

4.1.1 Unconditioned films

In this section, starch and chitosan blend films were tested without conditioning in humidifiers prior to measurements. After the fresh films were dried at ambient conditions, the films were tested for gas permeation.

The relative humidity of the films was approximately 40-80% under ambient conditions. The feed gas was humidified and therefore the humidity inside the permeation cell was slightly higher. From the range tested (0-90wt% chitosan), the permeabilities of N_2, O_2 and CO_2 were shown to be the lowest at a chitosan concentration of 60 - 70wt% in the starch-chitosan blends.

Because water can facilitate the transportation of the gases, when water vapor permeability is higher, the gas permeability should be higher as well. This is also due to the high solubility of CO_2 in water. Thus, at a higher water content, CO_2 permeability becomes higher comparing to N_2 and O_2 (i.e., higher selectivity of CO_2/N_2 and CO_2/O_2). Garcia *et al.* [2006] reported that the relative humidity in starch and chitosan blend films were generally lower than in individual component films at a given relative humidity of the gas. Also, the hydrogen bonds formed between starch and chitosan in the blend film may cause a decrease in gas permeability of the blend films comparing to films from individual component alone.

In the blend films, the permeability is 0.008 - 0.22 barrer for N_2, 0.02 - 0.58 barrer for O_2, and 0.32 - 10.99 barrers for CO_2 at different chitosan contents, as shown in Figure 4.1. The lowest permeability was observed at 67wt% chitosan, and the highest permeability was observed at pure starch film (without chitosan). This may be caused by the high hydrophilicity of starch. Starch films are more hydrophilic than chitosan, and contain a higher water content if they are exposed to gases at same relative humidity. A high water content facilitates gas permeation through hydrophilic films.
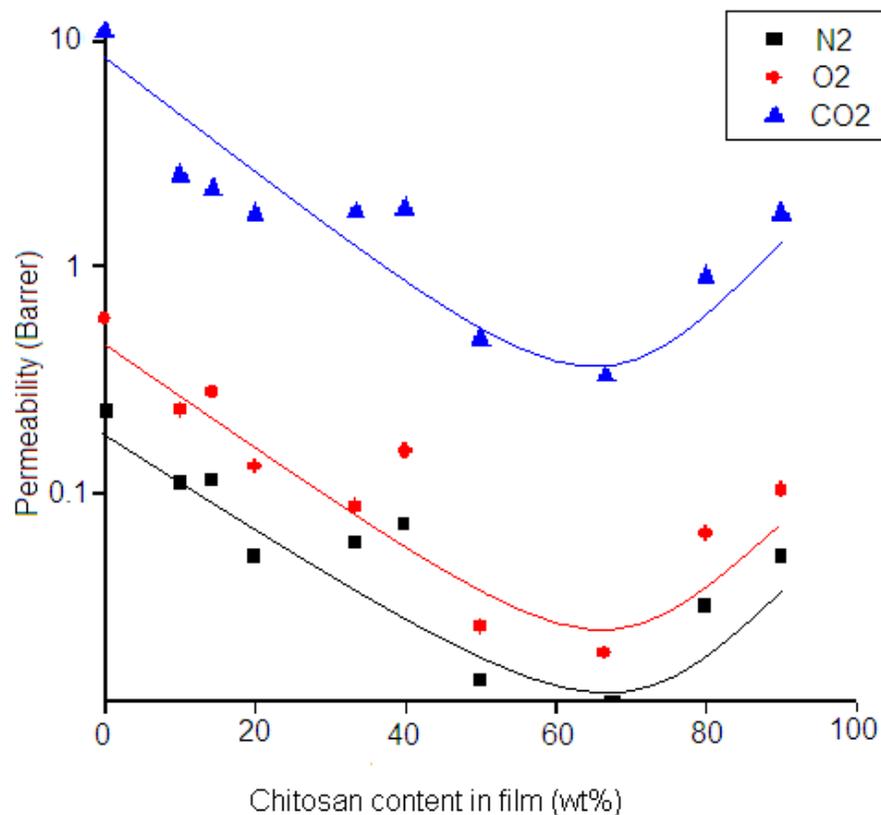
Figure 4.1 Gas permeability in unconditioned films with different chitosan contents

Figure 4.2 shows the selectivities of O_2/N_2, CO_2/O_2 and CO_2/N_2. The O_2/N_2 selectivity ranged from 1.4-2.6, the CO_2/N_2 selectivity varied from 19.7-49 and the CO_2/O_2 selectivity varied from 8-20.3. Interestingly, pure starch had a relatively high selectivity for CO_2/N_2, but the selectivity decreases when chitosan was added; when the chitosan content in the film is high enough, the selectivity begins to increase with chitosan content, resulting in a minimum at certain chitosan content in the film.
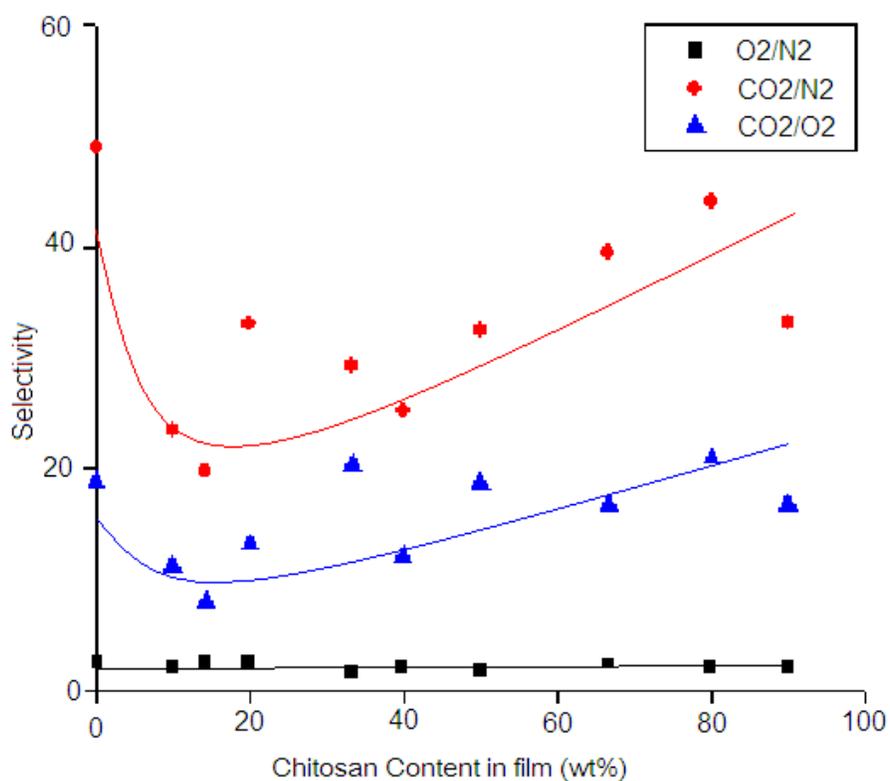
Figure 4.2 Selectivity of gases on unconditioned films with different chitosan contents

The variation of the permeations through unconditioned films was high due to the different relative humidity during film formation. It should also be pointed out that pure

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chitosan was not measured in this study, but starch-chitosan blend film with 90wt% chitosan was shown to be comparable with pure chitosan film from literature results. The CO_2 permeability (1.7 barrers) in the 90wt% chitosan blend film is between 0.85 barrer to 5.18 barrer reported by Despond *et al.* [2001] for pure chitosan films at different relative humidity.

4.1.2 Conditioned films
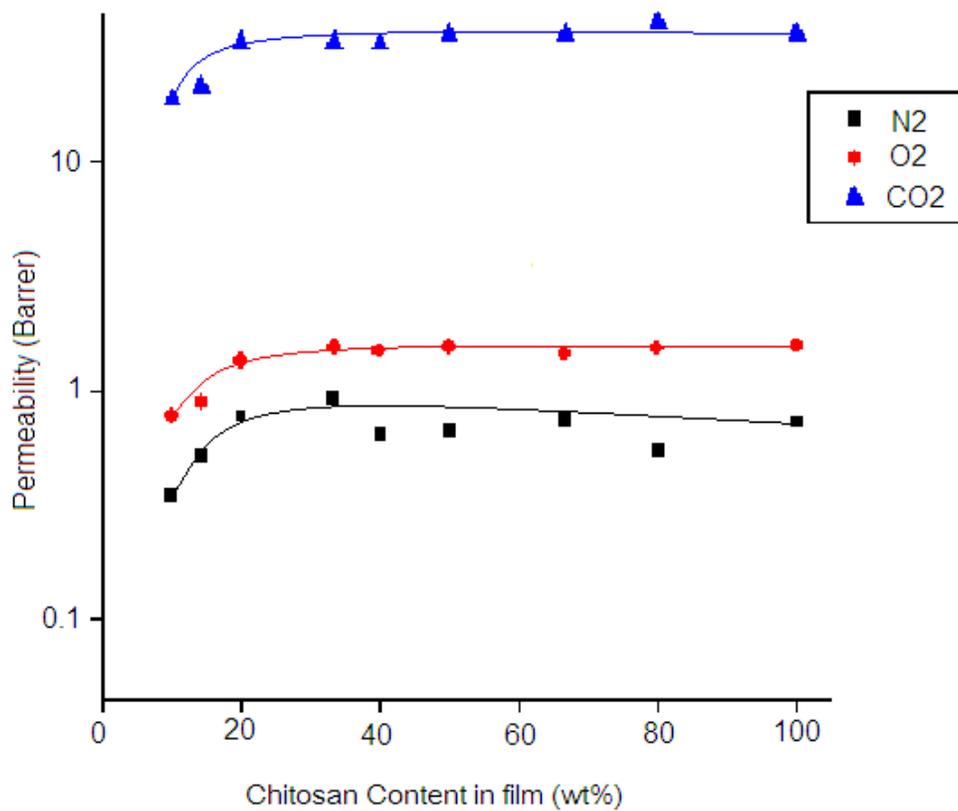
Figure 4.3 Gas permeability in conditioned films with different chitosan contents

In this section, the films were conditioned in a humidifier (~100% relative humidity) prior to permeability measurements. Pure starch film was not included in this study because

the starch film contained too much moisture and was not able to withstand the pressure during the permeability measurements. The permeability coefficients varied in the ranges 0.35 - 0.93, 0.78 - 1.58, and 18.73 - 40.01 barrers for N_2, O_2 and CO_2, respectively. When the chitosan content in the films increased from 10 to 33wt%, the permeabilities of all three gases increased; however, a further increase in the chitosan content did not have a significant effect on the gas permeability, as shown in Figure 4.3.
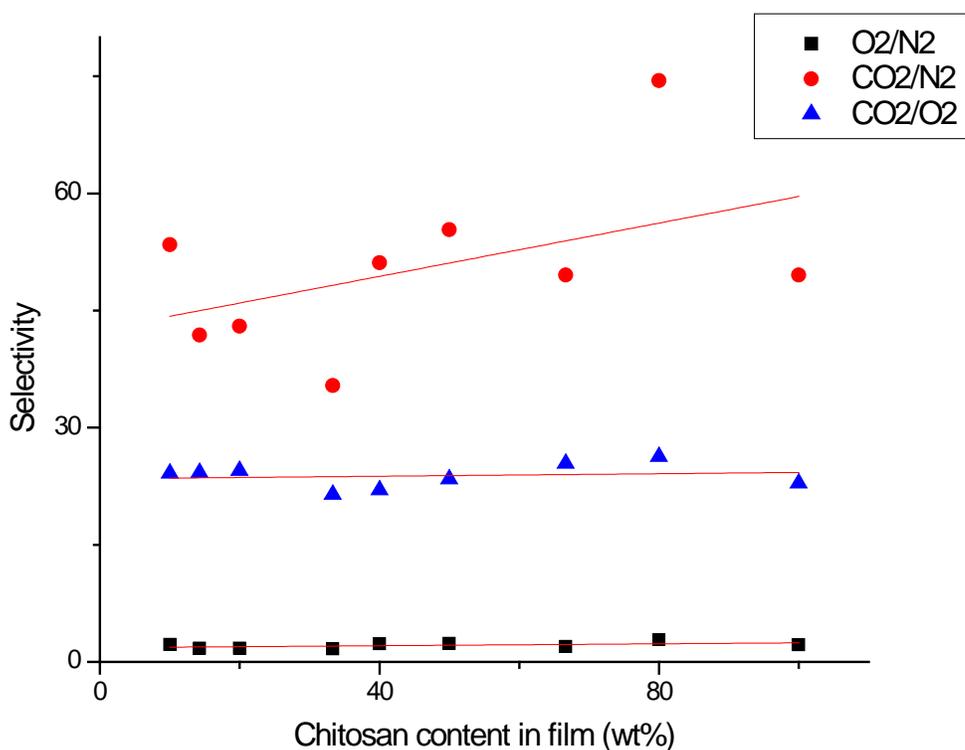
Figure 4.4 Selectivity of conditioned films with different chitosan contents

The selectivity of O_2/N_2 through the films is in the range of 1.6 - 2.8. The CO_2/N_2 selectivity increased with an increase in chitosan content in the films. Comparing to the

unconditioned films, the conditioned films had a slightly higher O_2/N_2 selectivity. Moreover, the CO_2/O_2 selectivity is also higher for conditioned films. The selectivity of CO_2/O_2, in the range of 21.5 – 26.3, was also found to be not significantly affected by the chitosan content in the films. The chitosan content has little effect on the gas permeability when the water content in the film is high. This is in agreement with the observation that when water content in the film is significantly high, the permeability tends to level off [Liu *et al.* 2008].

4.1.3 Effect of humidity

Comparing the permeability data obtained for the films with and without conditioning, it is clear that the conditioned films (humidified prior to testing) have higher permeability and selectivity. On average, the permeabilities of the conditioned films are 24.9, 25.4 and 36.5 times greater than the unconditioned film for N_2, O_2 and CO_2, respectively. It has been reported that starch films with 28wt% sorbitol had an increase in O_2 permeability by 6.5 times and 48.1 times when the relative humidity increased from 60- 80% and 60-90% respectively [Gaudin *et al.*, 2000]. For chitosan film, the permeability of O_2 and CO_2 increased by 3.5 and 28.3 times, respectively, when relative humidity increased from 0 to 96% [Despond *et al.*, 2001]. It was also found that the water content has a larger effect on CO_2 permeation than on to N_2 and O_2, which is in agreement with the solubility data in Table 4.1.

The gas permeability of conditioned pure chitosan film in this study is shown to be more permeable than that reported by Despond *et al.* [2001], who showed O_2 and CO_2

permeabilities of 0.31 and 5.18 barrers, respectively. A permeability of 1.57 and 36.0 barrers for O_2 and CO_2, respectively, was obtained in this study. The selectivity of CO_2/O_2 from this research is also higher (22.9) than the data of Despond *et al.* (16.7). This is believed to be due to the different conditions used during membrane formation. The chitosan film used by Despond *et al.* was neutralized after film formation, while the chitosan used in this study was in the form of chitosanium salt. What is more, the operating pressure used was higher in this research than that used by Despond *et al.* [2001], and this may also affect the gas permeability. Table 4.2 summarizes the gas permeability and selectivity of chitosan films at different operating conditions.

Table 4.2 Summary of gas permeability in chitosan films

Temperature	Pressure	relative humidity	CO_2 Permeability	CO_2/N_2 Selectivity	CO_2/O_2 Selectivity	Reference
n/a	22	n/a	0.26	5.63	3.10	Sathivel *et al.*,
20	43	0	0.03	N/A	1.25	Despond *et al.*, 2001
		96	0.85	N/A	10.24	
		100	5.18	N/A	16.71	
25	60	Swollen by	36.00	49.5	22.90	This work
20	35-115	Water-	~200	45-54	N/A	Liu *et al.* 2008
N/A	115	swollen	~200	40-60	N/A	
Room temp	N/A	Swollen by		70*	N/A	Ito *et al.*,

   *Mixed gas

Liu *et al.* [2008] also measured gas permeability in dry and water-swollen chitosan membranes and found that the permeability of N_2 and CO_2 in water swollen chitosan film is

10,000 times greater than the gas permeability in dry chitosan films. This present study also showed that chitosan films swollen by feed gas (which is less hydrated than water swollen films) had a permeability much higher than that of the dry chitosan films. The same trend is found for the selectivity of CO_2/N_2 which increased more for water-swollen chitosan than from dry chitosan. This can be explained by the water content difference in the films.

Ito *et al.* [1997] reported the permeability and selectivity of CO_2 and N_2 using mixed gases, and the data are quite close to the results obtained in this study with pure gases (i.e., CO_2 and N_2).

4.2 Effect of Pressure

To investigate the effect of pressure on the gas permeability, films containing 0, 20, 40, 60 and 100wt% chitosan were tested at different cross membrane pressures (20, 40, 60, 80, and 100 psi).

Figure 4.5 shows the N_2 permeability in films with different chitosan contents as a function of pressure. The permeation of N_2 through chitosan and starch-chitosan blend membranes increased with an increase in pressure. As mentioned previously, chitosan concentration did not affect the N_2 permeability when the chitosan content in the blend films varied from 20 to 100wt%. As shown in Figure 4.5, the N_2 permeabilities of the blend films at 20, 40, and 60wt% chitosan were very close. It is also shown that the pressure has a more significant effect on the gas permeability through chitosan films, while the effect for other films (i.e., starch films, starch-chitosan blend films) is less significant.

The above results may be due to the difference in the molecular structures of starch and chitosan. As mentioned in chapter 2, starch is not uniform and contains two types of complex carbohydrate polymers of glucose [Gregorová *et al.,* 2006; Rdríguez *et al.,* 2006; Zobel and Stephen, 2006]. Amylose is linear and amylopectin is branched. The combination of the two makes the film a better barrier to gas permeation. The starch-chitosan blend films have hydrogen bonds between starch and chitosan [Xu *et al.*, 2005] which makes the molecular structure denser. Pure chitosan, on the other hand, has only one type of linear molecule; and therefore, is more favorable to gas permeation.
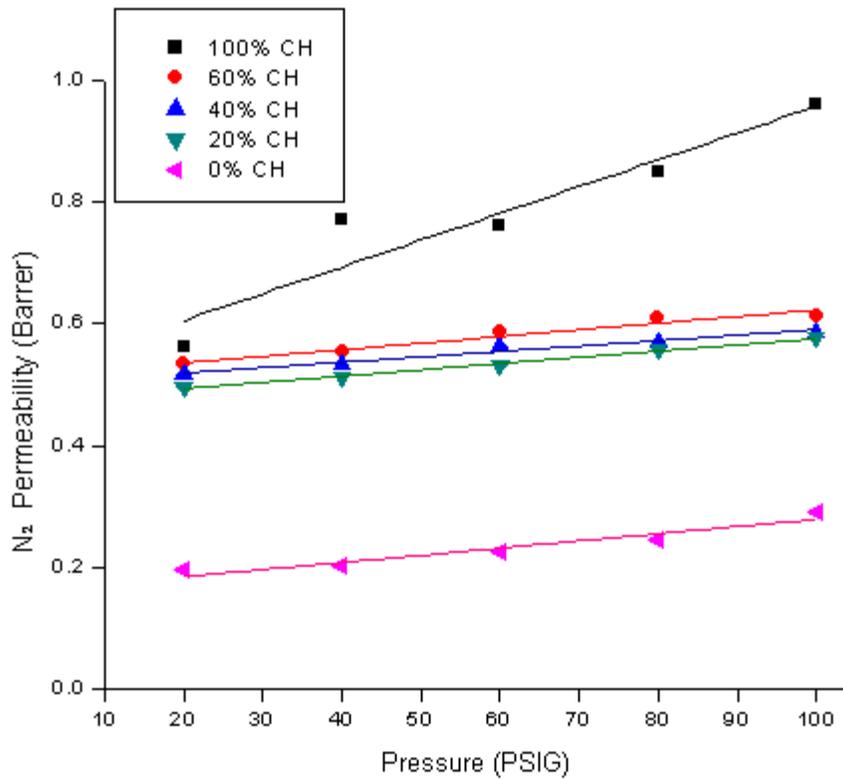
Figure 4.5 Permeability of N_2 in films with different chitosan contents at different pressures

The effect of cross membrane pressure on the permeation of O_2 is similar to that of N_2. The permeability of pure starch film was lower than the permeabilities of starch-chitosan blend films, as shown in Figure 4.6. The gas pressure has a similar effect on the permeability of the starch-chitosan blend films and the starch films, while the effect of cross membrane pressure is more significant on the gas permeability of chitosan film. The same trend has been observed for the N_2 permeability. It indicates that the starch, chitosan, and starch-chitosan blend films all follow the basic solution-diffusion interactions with N_2 and O_2.
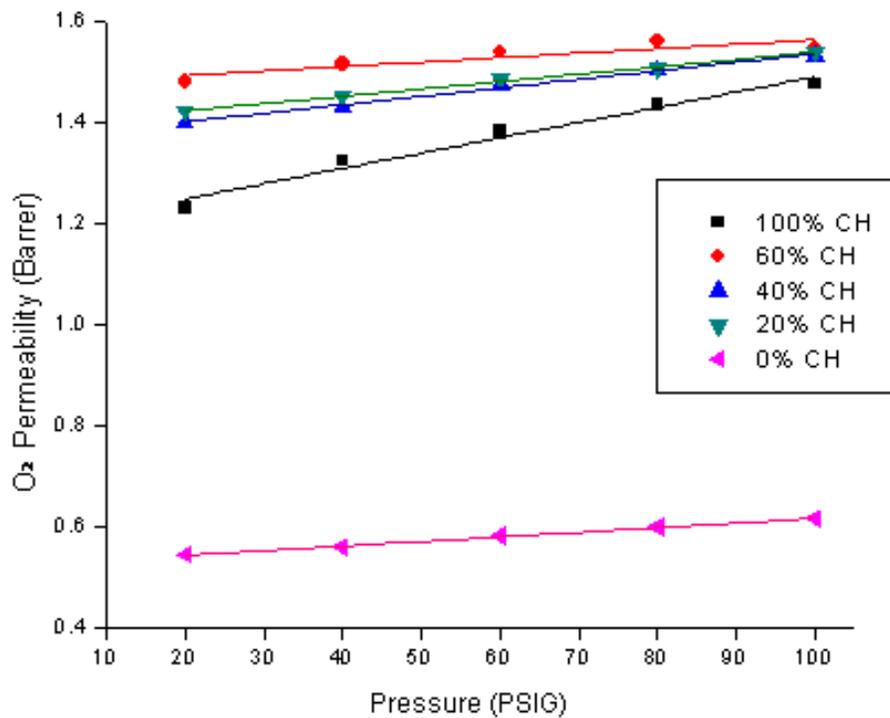
Figure 4.6 Permeability of O_2 in films with different chitosan contents at different pressures

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Crosslinking is a process of connecting two or more molecules by forming a bond between them. As stated earlier, inter-molecular hydrogen bonds are formed between starch (OH^-) and chitosan ($-NH_3$) [Xu *et al.*, 2005]. This inter-molecular interaction between starch and chitosan may be considered to have an effect similar to crosslinking. Liu *et al.* [1999] reported on the gas permeabilities of N_2, H_2, and O_2 in crosslinked and uncrosslinked polyimides. It was found that the higher the degree of crosslinking , the lower the gas permeability. Crosslinking improves the gas barrier properties of membranes. Also the permselectivities of H_2/N_2 and O_2/N_2 both increase with an increase in the degree of crosslinking. Similar results were obtained on crosslinked polyimide membranes at different cross membrane pressures by Wind *et al.* [2002]. In the pressure range tested (20-320psia), the uncrosslinked membranes had a higher permeability of CO_2 and lower CO_2/CH_4 selectivity than the crosslinked membrane. The change in starch-chitosan film permeability here is not as high as the chemically crosslinked polyimide membranes, presumably due to the weak hydrogen bonding compared to covalent or ionic bonds.

The permeation behavior of CO_2 through starch-chitosan films is different from that of N_2 and O_2. The permeability of CO_2 decreased with an increase in pressure, which is the opposite as compared to the permeation of N_2 and O_2. As mentioned earlier, the permeation of CO_2 in the films containing chitosan is not a simple solution-diffusion process. Because CO_2 is an acidic gas, there is a weak acid-base interaction between water and CO_2; therefore CO_2 has a high solubility in water. The flux of CO_2 at low pressure is mainly attributed to solubility. When the cross membrane pressure increases, the flux still increases, but the flux

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increase is less than proportional comparing to the contribution from acid-base interactions, resulting in a decrease in the permeability coefficient as the pressure increases. This is supported by the fact that CO_2 solubility coefficient in water tends to decrease when the pressure increases, although the CO_2 sorption uptake still increases with the pressure.
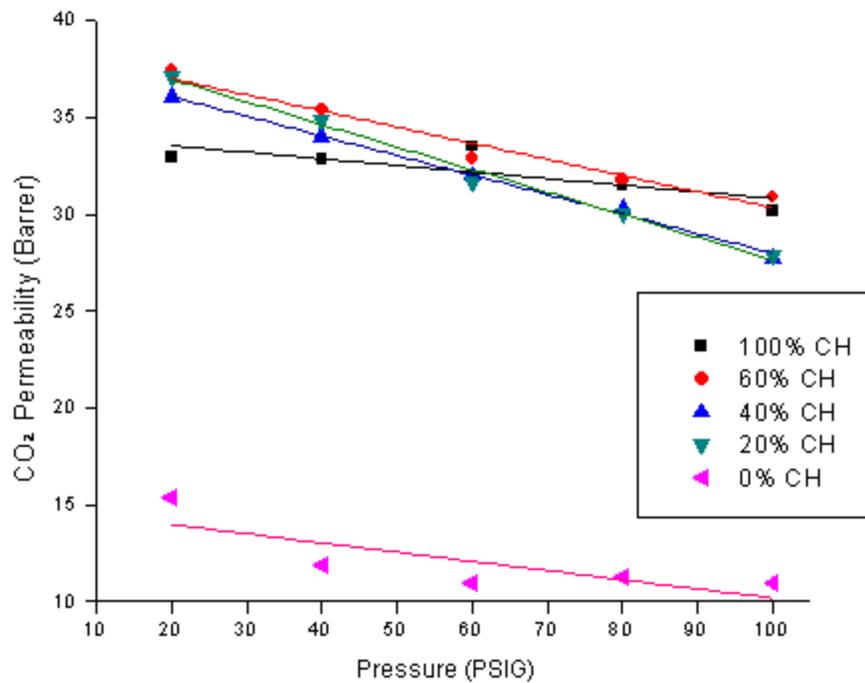
Figure 4.7 Permeability of CO_2 in films with different chitosan contents at different pressures

Moreover, since chitosan has hydroxyl groups, the attraction between CO_2 and chitosan film swollen by water is even stronger. As seen from Figure 4.7, the decrease in CO_2 permeability is less significant for pure chitosan film than for blend films and starch

films. This is understandable because the interaction between CO_2 and chitosan film having a high water content is so strong that a change in pressure does not have a significant effect on the permeability coefficient. Similar behavior was also noticed by Liu *et al.*[2008] where hydrogel membranes (water-swollen chitosan membranes) have only a slight decrease in permeability when the pressure increases. It was also shown that the decrease in permeability is partially due to the compaction of soft hydrogel membrane under high pressures [Liu *et al.*, 2008].

Since starch is more hydrophilic than chitosan, starch films have higher water content than chitosan films at a given relative humidity in the gas. The interaction between CO_2 and water-swollen starch film will be stronger than with blend films. However, because it doesn't have the basic property, the interaction with CO_2 is weaker than the CO_2- chitosan interaction.

Figure 4.8 shows that the O_2/N_2 selectivity decreases with an increase in the gas pressure because N_2 permeability increased more significantly with pressure than O_2 permeability. The chitosan film has the lowest O_2/N_2 selectivity, ranging from 1.54 to 2.19, and the starch film has a slightly higher selectivity (2.11 – 2.80). Similar selectivity was observed (2.52 – 2.86) with the starch-chitosan blend films. Nevertheless, the pressure tends to have a higher effect on the single component films. The permeability of blend films was less affected by the cross-membrane pressure. As mentioned before, the blend films may have less "free volume" due to the bonds between starch and chitosan which acts in a manner similar to crosslinking.
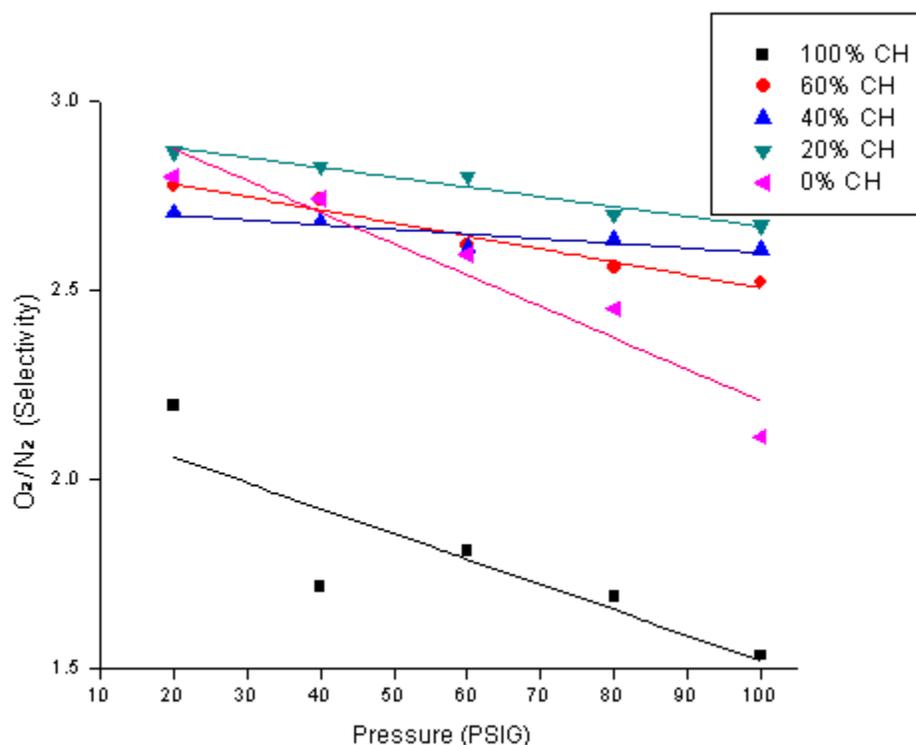
Figure 4.8 Selectivity of O_2/N_2 in films with different chitosan contents at different

pressures

Figure 4.9 shows the selectivity of CO_2/N_2 in the films, and a similar trend to the O_2/N_2 selectivity can be observed. The selectivity decreased with an increase in the cross membrane pressure. Chitosan film (31.4 - 58.8) and starch film (37. 6 - 58.1) have similar selectivities except starch film at 20 psig (79.04). The blend films tend to have a higher selectivity, which ranged from 47.3 to 75.0. For the blend films with different chitosan content, it can be found that the lower the chitosan content in the starch-chitosan blend film, the stronger the effect of pressure on the film selectivity.
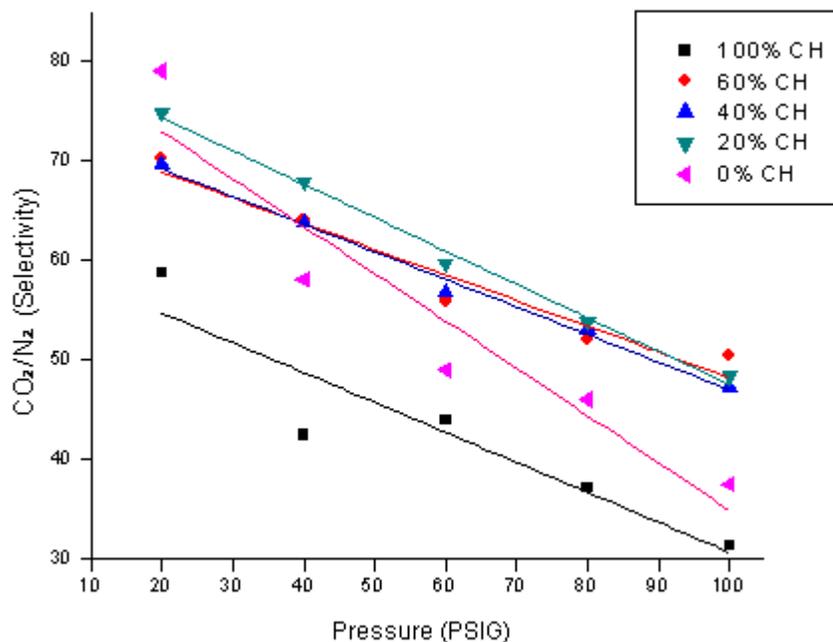
Figure 4.9 Selectivity of CO_2/N_2 in films with different chitosan content at different

pressure

Figure 4.10 showed the CO_2/O_2 selectivity in the films with different chitosan

contents at different cross membrane pressures. As both O_2 and N_2 exhibited a similar

permeation behavior, the CO_2/O_2 selectivity is shown to have a similar trend as the CO_2/N_2

selectivity where the effect of pressure is the most significant on pure starch films.

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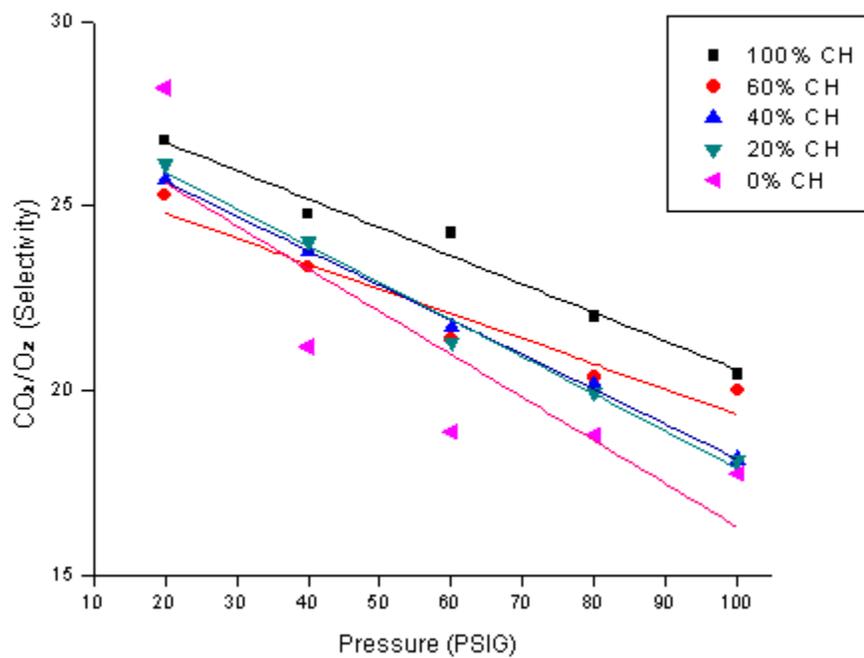
Figure 4.10 Selectivity of CO_2/O_2 in films with different chitosan contents at different

pressures

4.3 Effect of Temperature

To evaluate the temperature dependence of the permeability, the gas permeation

through the various films were tested at different temperatures ranging from 20 to 40°C. The

gas permeabilities of N_2, O_2 and CO_2 all increased with an increase in temperature, and the

temperature dependence of permeability was shown to follow the Arrhenius relationship,

from which the activation energy of permeation was calculated. The activation energy of

permeation defines the energy barrier that needed to be overcome for molecules to permeate through the membrane.

4.3.1 Chitosan film

The effect of temperature on the gas permeability in chitosan film is shown in Figure 4.11. Please note that two sets of data from two chitosan films under the same operating procedure are presented in the figure in order to show the consistency of the results obtained. From the average of three measurements, N_2 permeability increased from 0.64 to 1.0 barrer when temperature increased from 20 to 40˚C. The activation energy of permeation was calculated using Equation 3.3. The activation energy of N_2 permeation in chitosan film was found to be 16.7 kJ/mol. O_2 permeability was found to increase from 1.48 to 1.82 barrer with an activation energy of 7.6 kJ/mol. CO_2 permeability increased from 30.0 barrer to 35.1 barrer and the activation energy of permeation is 5.99kJ/mol. The activation energy of permeation through chitosan membrane is summarized in Table 4.3.

Table 4.3 Activation energy of permeation on chitosan film

Condition	Temperature ˚C	N_2 kJ/mol	O_2 kJ/mol	CO_2 kJ/mol	Reference
Dry	20-150	44.9*	N/A	34.1*	El-azzami and Grulk, 2007
Water-saturated feed gas	20-40	16.7	7.6	5.99	This work
Water swollen	23-60	21.3	N/A	6.6	Liu *et al.*, 2008

*mixed gas

El-azzami and Grulk [2007] obtained the activation energy of for gas mixture permeation in dry chitosan films. It was found that the dry chitosan film has a higher activation energy of permeation than moist chitosan films. Liu *et al.*[2008] reported the activation energy of N_2 and CO_2 in water-swollen chitosan films, which is 21.3 and 6.58 kJ/mol for the permeation of N_2 and CO_2, respectively. They are similar to the values obtained in this study, although the membranes were treated differently. Nevertheless, for all conditions (dry, saturated feed gas, and water-swollen), the activation energy of N_2 permeation is higher than the activation energy of CO_2 permeation.
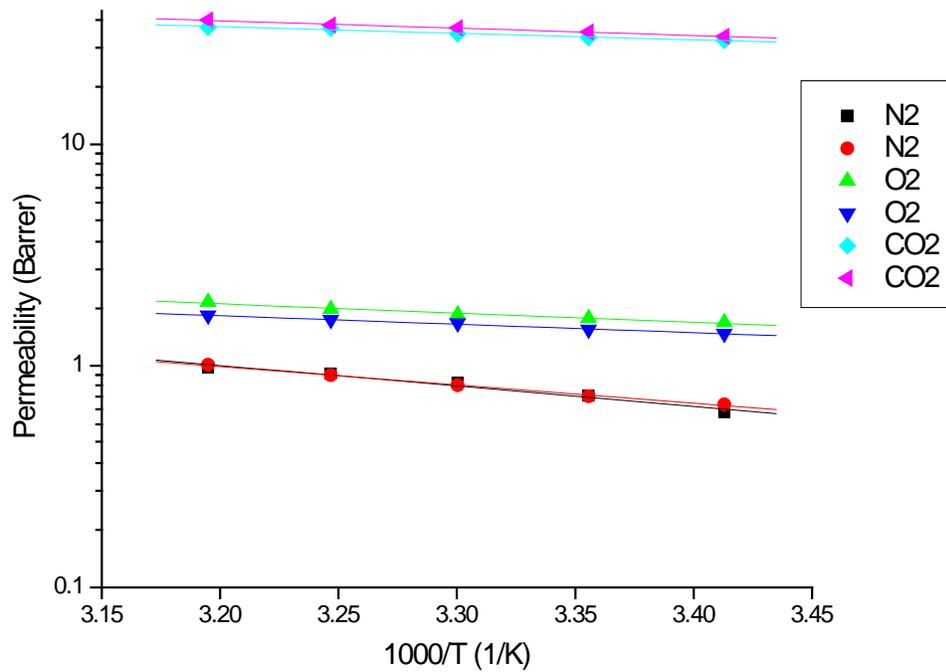
Figure 4.11 N_2, O_2 and CO_2 permeability in chitosan film at different temperatures

The selectivity of CO_2/N_2, O_2/N_2 and CO_2/O_2 all decreased with an increase in temperature. The selectivity of CO_2/N_2 and O_2/N_2 decreased more significantly with an increase in temperature than the CO_2/O_2 selectivity. From the activation energy and the decrease in selectivity, it can be found that temperature has a greater effect on N_2 permeation than on O_2 and CO_2. The activation energy of permeation is in the order of $N_2 > O_2 > CO_2$. In general, the less permeable gas tends to have a higher activation energy for permeation.

4.3.2 Starch and chitosan blend films

The temperature dependence of gas permeabilities in the starch-chitosan blend films had the same trend in chitosan films. Figure 4.12 – 4.14 show the permeabilities of N_2, O_2 and CO_2 in the starch-chitosan blend films at different temperatures. In general, the temperature has a significant influence on gas permeability, and the temperature dependence of the permeability follows the Arrhenius relation. The activation energy of permeation was determined, as shown in Figure 4.15. Appendix D shows detailed activation energy of the blend films with different chitosan contents. It appears that as the chitosan content in the blend film increases, the activation energy increases initially and then decreases when the chitosan content is sufficiently high, resulting in a maximum activation energy at a certain film composition. The maxima are more obvious for the less permeable gases (also the gases with higher activation energy of permeation). The maximum activation energy of permeation for the gases seems to occur at around 50-70wt% chitosan in the blend membranes. This is fairly close to film composition (60-70wt% chitosan) at which a minimum permeability was observed previously at ambient conditions.
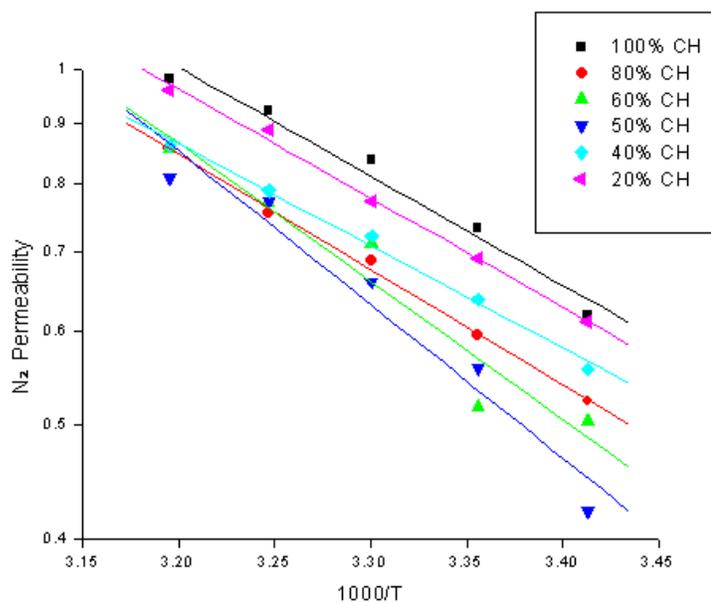
Figure 4.12 N_2 permeability in films with different chitosan contents at different temperatures
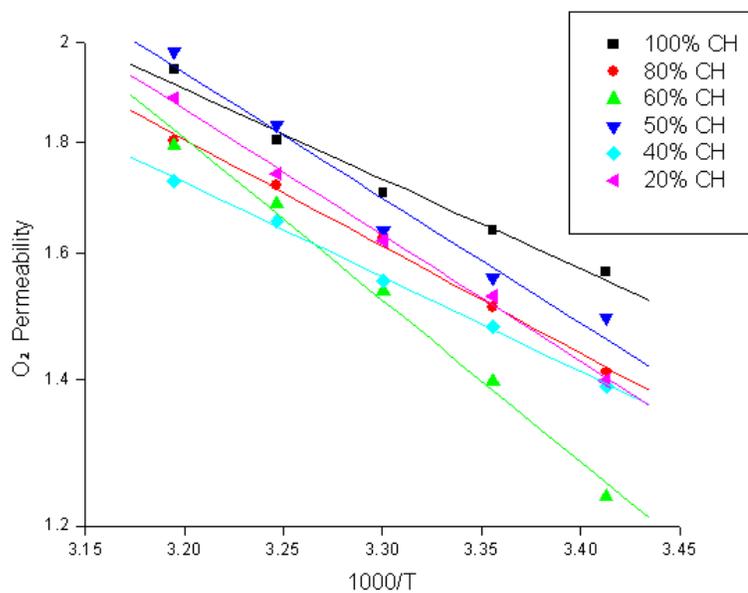
Figure 4.13 O_2 permeability in films with different chitosan contents at different temperature
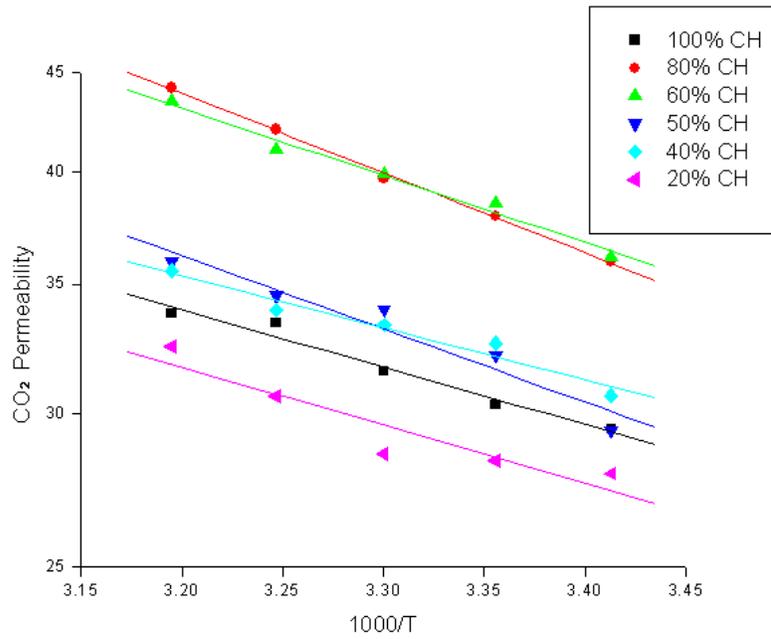
Figure 4.14 CO_2 permeability in films with different chitosan contents at different temperature
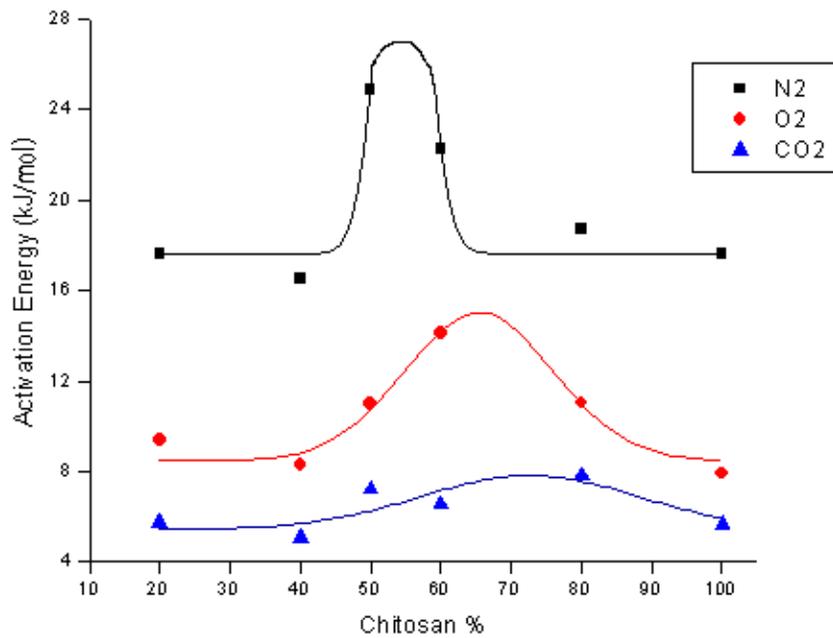
Figure 4.15 Activation energy for films with different chitosan contents

The activation energy for the permeation of N_2, O_2 and CO_2 through PU/PMMA (polyurethane/poly methylmethacrylate) films has been reported to be 40.4, 36.9, and 26.4 kJ/mol for N_2, O_2, and CO_2, respectively [De Sales *et al.*, 2008]. The higher activation energy of permeation indicates that temperature has a larger effect on the gas permeation. The same trend was found on PU/PMMA film for which the activation energy is in the order of $N_2 > O_2 > CO_2$. A summary of comparisons of the activation energy through different membranes is presented in Table 4.4, which shows that the starch-chitosan films have an activation energy comparable to other membranes made of synthetic polymers. As seen in Table 4.4, CO_2 in general has a lower activation energy of permeation than N_2 and O_2.

Table 4.4 Comparison of activation energy of permeation on different membranes

Material	N_2 kJ/mol	O_2 kJ/mol	CO_2 kJ/mol	Reference
PU	26.4	36.9	40.4	De sales *et al.*, 2008
PC	6.0	5.0	3.0	Costello and Koros, 1994
TMPC	4.0	2.8	1.6	
TMHFPC	3.0	2.1	0.4	
6FDA-6FpDA	3.2	2.0	0.7	Costello and Koros, 1995
6FDA-6FmDA	5.4	3.1	2.2	
6FDA-durene	4.5	2.4	0.2	Lin and Chung, 2001
Chitosan	21.3	N/A	6.6	Liu *et al.*, 2008
Chitosan	17.6	7.9	5.7	This work
Corn starch + Chitosan (1:1)	24.9	11.0	7.2	

The selectivities of O_2/N_2, CO_2/N_2 and CO_2/O_2 are presented in Figure 4.16 – 4.18. The selectivities of O_2/N_2 and CO_2/N_2 decreased with an increase in temperature. The

decrease in selectivities was most drastic at 50 and 60wt% chitosan for O_2/N_2 and CO_2/N_2, respectively. The variation in selectivity of CO_2/O_2 with chitosan content is more moderate except for the film containing 50wt% chitosan. This corresponds to the fact that the permeability coefficients for N_2, O_2 and CO_2 were the lowest at around 60wt% chitosan in the unconditioned starch-chitosan blend films as shown previously (see section 4.1). Similar trend was found in section 4.3 with respect to the activation energy of permeation. Because of the higher activation energy of films with 50 - 60wt% chitosan, they are more sensitive to temperature change and therefore selectivity decreased significantly with an increase in temperature.
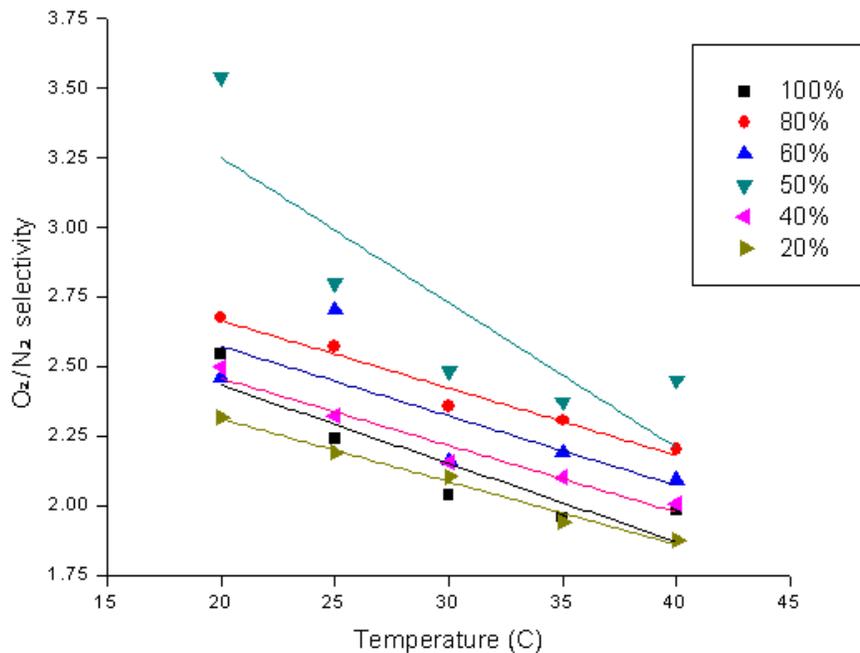
Figure 4.16 O_2/N_2 selectivity in films with different chitosan contents
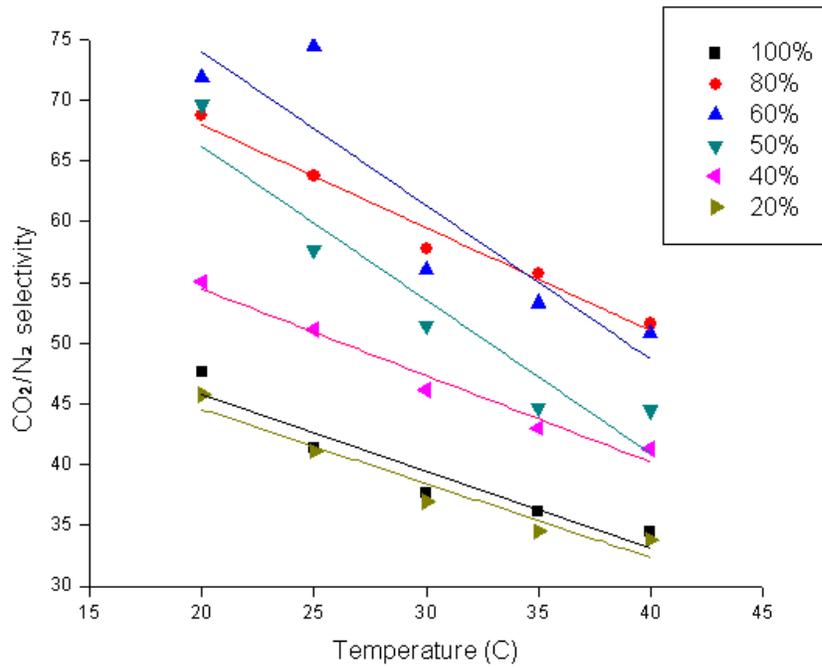
Figure 4.17 CO_2/N_2 selectivity in films with different chitosan contents
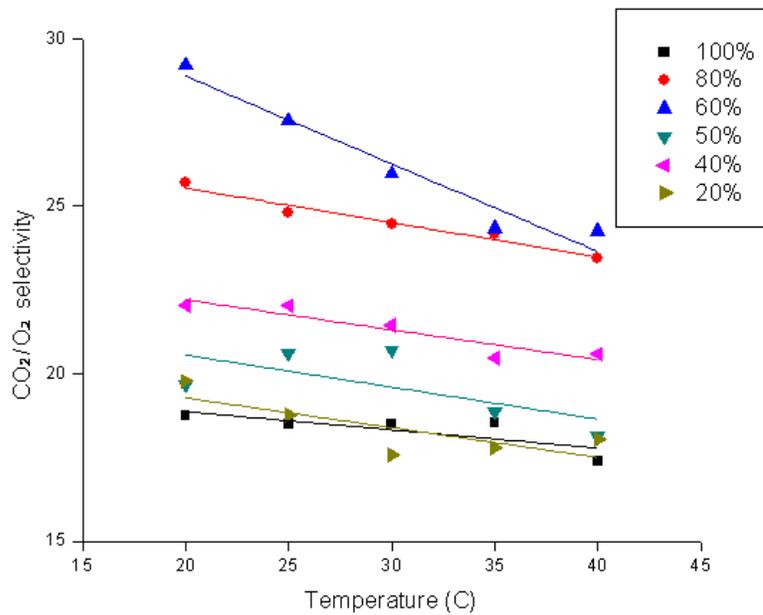
Figure 4.18 CO_2/O_2 selectivity in films with different chitosan contents

4.4 Comparison with traditional food packaging material

The common material for food packaging are PE (polyethylene), PVC (Polyvinyl chloride), LDPE (low density polyethylene) and many other types. They are used in plastic sandwich bags and saran wraps. The N_2, O_2 and CO_2 gas permeability of these materials are shown in Table 4.5. The unconditioned (not pre-humidified) starch-chitosan film with the lowest gas permeability is presented for comparison.

As comparing to polyethylene, the starch-chitosan blend film with 67wt% chitosan under ambient condition has much better gas barrier properties. The CO_2/N_2 selectivity also favors the permeation of CO_2 which is desired for packaging food containing fat (i.e., meat). Poly(ethylene oxide) is under research for CO_2 separation by Lin *et al.*[2005]. It can be found that the blend film obtained from this work is less permeable than the poly(ethylene oxide) polymer by Lin *et al.*[2005] with similar selectivities.

Table 4.5 Gas permeability of food packaging material

Material	N_2 Barrer	O_2	CO_2	O_2/N_2	CO_2/N_2	CO_2/O_2	Reference
Polyethylene	1.00	N/A	13.00	N/A	13	N/A	Lin *et al.*, 2005
Poly(ethylene oxide)	0.25	~0.70	12.00	~2.8	48	~17	
Poly(ether-b-amide)	N/A	N/A	120	N/A	N/A	N/A	Bondar *et al.*
Starch+Chitosan (67wt% Chitosan)	0.008	0.02	0.32	2.4	39.4	16.6	This work

Chapter 5
Conclusions and Recommendations

The permeabilities of N_2, O_2 and CO_2 gases in starch, chitosan and starch-chitosan blend films with different chitosan contents were determined at various cross membrane pressures and temperatures. For a given film, the gas permeability is in the order of $CO_2 > O_2 > N_2$, which is in the same order as their solubility in water. The acid-base interaction between CO_2 and chitosan favors the permeation of CO_2 in preference to other gases.

When the films are conditioned in a humidifier, their gas permeabilities were significantly enhanced. The unconditioned films have much better gas barrier properties than conditioned films. It was found that the higher the relative humidity, the higher the gas permeability. The pure starch film has the highest permeability at given operating pressures and temperatures, while the starch-chitosan blend films exhibited the lowest permeability when the chitosan content in the film is around 60-70wt%. The CO_2/N_2 and CO_2/O_2 selectivities both increased with an increase in chitosan content, while the O_2/N_2 selectivity did not change significantly.

For films conditioned prior to permeation measurements, the permeability of all three gases increased when chitosan content in the films increased from 10 to 33wt%; a further increase chitosan content did not have a significant effect on the permeability. The O_2/N_2 and CO_2/O_2 selectivities did not change with chitosan content, while the CO_2/N_2 selectivity significantly increased with chitosan content. On average, conditioned films were 25-36

times more permeable than unconditioned films. It was found that the chitosan content in the films had little effect on the gas permeability when the water content in the film was sufficiently high.

When the cross membrane pressure increased, N_2 and O_2 permeabilities increased while CO_2 permeability decreased. The increase in pressure had a greater effect on the permeation of N_2 and O_2 in pure chitosan film. This is due to the inter-molecular hydrogen bonds between starch (OH^-) and chitosan ($-NH_3$) in blend films. The CO_2 permeability, on the other hand, decreased with an increase in pressure because of the interaction between acidic CO_2 and basic chitosan. It is also found that the effect of pressure on CO_2 permeability was smaller at a higher chitosan content.

Temperature was found to have a significant effect on the gas permeability, and the temperature dependence of permeability followed the Arrhenius relationship. The activation energy for the permeation of the three gases was in the order of $N_2 > O_2 > CO_2$. The activation energy of permeation was also affected by the film composition. The activation energy for the gases tends to reach a maximum at around 60wt% chitosan. This corresponds to the lowest permeability at ambient temperature and 60psig.

Even though corn starch films may have better barrier properties under some conditions, the film is brittle and lack good mechanical properties. Addition of plasticizer would increase the flexibility of the film but the gas permeability would also increase. It was found that by blending corn starch and chitosan, the barrier property was better than the films of either single component alone. With the addition of chitosan, not only was the gas barrier

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property improved, the blend films also decayed much slower than the starch film at high

relative humidity due to the antimicrobial property of chitosan. It is recommended that the

starch-chitosan films be further investigated with respect to their mechanical properties such

as tensile strength, and applications of these starch-chitosan blend films on real fruit/meat can

be tested as some similar work using protein or gelatin films has been carried out in the

literature. This will allow for evaluation of the blend films for actual applications in

comparison with the packaging films that are used currently.

Nomenclature

C	Concentration	mol/m^3
F	Flux	$cm^3(STP)/(cm^2.s)$
J	Permeance	$cm^3(STP)/(cm^2.s.cmHg)$
l	Thickness of membrane	m
P	Permeability coefficient	$cm^3(STP).cm/(cm^2.s.cmHg)$
Δp	Cross membrane pressure	cmHg
Q	Quantity of permeant	mol or $cm^3(STP)$
S	Effective area	cm^2
T	Temperature	˚C or ˚K
t	Time	s
α	Selectivity	

Conversions to conventional units

1 GPU	$= 10^{-6} cm^3(STP)/(cm^2.s.cmHg)$
1 barrer	$= 10^{-10} cm^3(STP).cm/(cm^2.s.cmHg)$
1 mol	$= 22400 cm^3 (STP)$

Appendices

Appendix A

Permeation Comparison Table

The tables below summarize the N_2, O_2 and CO_2 gas permeabilities and water vapor permeability in starch (A.1 and A.2), chitosan (A.3 and A.4) , starch-chitosan blend (A.5), and other similar films (A.6 and A.7). Some of the data were mentioned earlier in chapter 2 and chapter 4 for comparison with other literature data or data from this research work. Sometimes the literature data are reported without specifying the conditions and if this is the case, they will be marked as N/A (not available).

Table A.1 Literature data of O_2 permeability in starch films under different conditions

Starch type	Plasticizer	Temperature	Relative Humidity	O_2 Permeability	Reference
100	Glycerol (40%)	n/a	50	0.011	Rindlav-Westling *et al.*, 1998
0				0.022	
100	Glycerol (30%)	20	50	0.002	Forssell *et al.*, 2002
0				0.003	
25	Glycerol (12%)	n/a	50	0.002	Dole *et al.*, 2004
	Glycerol (18%)			0.005	
	Glycerol (25%)			0.014	

(continued)

Starch type % amylose	Plasticizer	Temperature ˚C	Relative Humidity %	O$_2$ Permeability Barrer	Reference
27	Sorbitol (0%)	20	57	0.00187	Gaudin *et al.*, 2000
	Sorbitol (8.8%)			0.00019	
	Sorbitol (16.2%)		N/A	0.00036	
	Sorbitol (20.0%)			0.00043	
	Sorbitol (21.0%)			0.00041	
	Sorbitol (24.3%)			0.00193	
	Sorbitol (28.0%)			0.00173	
	Sorbitol (8.8%, 28%)		57	0.0003,0.0028	
			60	0.0008,0.0259	
			70	0.0036,0.0258	
			80	0.0057,0.1696	
			90	0.0017,1.2461	

Table A.2 Literature data of water vapor permeability of starch films under different conditions

Starch type % amylose	Plasticizer	Relative humidity %	Water Vapor Permeability g/m.day.atm			Reference
100	Glycerol (40%)	50-85	10.436			Rindlav-Westling *et al.*, 1998
0		50-85	12.564			
100	Glycerol (40%)	1-53	0.476			Rankin *et al.*, 1958
0		29-81	2.330			
Potato	None	0-33, 0-54, 0-76	0.107	0.287	0.304	Talja, *et al.* 2007
	Glycerol (20%)		0.049	0.097	0.140	
	Glycerol (30%)		0.127	0.198	0.372	
	Glycerol (40%)		0.333	0.454	0.613	
	Xylitol (30%)		0.012	0.046	0.114	
	Xylitol (40%)		0.025	0.089	0.160	
	Sorbitol (40%)		0.007	0.035	0.099	
	Sorbitol (50%)		0.014	0.078	0.196	
Cassava	Glycerol (25%)	2-33, 33-64, 64-90	0.387	0.598	2.456	Müller *et al.*, 2008
	Glycerol (30%)		0.567	0.834	2.505	
	Glycerol (35%)		0.588	1.075	2.529	
	Sorbitol (25%)		0.119	0.124	0.204	
	Sorbitol (30%)		0.143	0.143	2.142	
	Sorbitol (35%)		0.184	0.198	2.361	

Table A.3 Literature data of gas permeability in chitosan films under different conditions

Temperature °C	Pressure psig	Relative Humidity %	Permeability Barrer			Selectivity		Reference
			N_2	O_2	CO_2	CO_2/N_2	CO_2/O_2	
20-150	22	Dry			0.381-26.1*	19.7-4.55*	3.14 – 1.71* (/H_2)	El-azzami and Grulke, 2007
	29	Dried at 35%	0.046	0.081	0.259	5.63	3.1	Sathivel et al., 2007
25		0	N/A	0.011	N/A	N/A	N/A	Caner et al.,1998
Room temp		Swollen by feed gas	N/A	250*	N/A	70*	28* (/CH_4)	Ito et al., 1997
20	43	0	N/A	0.024	0.03	N/A	1.25	Despond et al., 2001
		31	N/A	N/A	0.05	N/A	N/A	
		58	N/A	N/A	0.06	N/A	N/A	
		82	N/A	N/A	0.12	N/A	N/A	
		91	N/A	N/A	0.36	N/A	N/A	
		96	N/A	0.083	0.85	N/A	10.24	
		98	N/A	0.16	1.16	N/A	7.25	
		100	N/A	0.31	5.18	N/A	16.71	
25	35-115	Water-swollen	4-5	N/A	~200	45-54	N/A	Liu et al. 2008
22.5-60	115	N/A	2-5	N/A	~200	40-60	N/A	

*Mixed gas

Table A.4 Literature data of water vapor permeability in chitosan films under different conditions

Temperature ˚C	Pressure psig	Relative Humidity %	Water Vapor Permeability g/m.day.atm	Reference
n/a	29	10-90	2.56	Sathivel *et al.*, 2007
25	n/a	50% difference	0.831	Caner *et al.*, 1998

Table A.5 Literature data of water vapor permeability in starch-chitosan blend films under different conditions

Chitosan %	Plasticizer	Temperature ˚C	Relative Humidity %	Water Vapor Permeability g/m.day.atm	Reference
0	none	20	0-75	1.156-1.856	Garcia *et al.*, 2006
14-22	Glycerol (28%)		N/A	0.329-0.397	
100	none			0.394	

Table A.6 Literature data of gas permeability in chitosan and gelatin blend films under different conditions

Material	Plasticizer	Temperature	N_2 Permeability Barrer	O_2 Permeability Barrer	CO_2 Permeability Barrer	CO_2/N_2 Selectivity	CO_2/O_2 Selectivity	Reference
Chitosan + Gelatin	None	Cast at 22°C	0.017	0.003	0.075	4.3	23.3	Arvanitoyannis *et al.*, 1998
	Glycerol (4%)		0.040	0.005	0.115	2.9	21.0	
	Glycerol (17%)		0.853	0.187	3.200	3.8	17.1	
	Sorbitol (5%)		0.020	0.006	0.111	5.5	17.3	
	Sorbitol (14%)		1.080	0.253	4.667	4.3	18.4	
	None	Cast at 60°C	0.227	0.033	0.867	3.8	26.0	
	Glycerol (4%)		0.453	0.059	1.200	2.6	20.5	
	Glycerol (15%)		2.667	0.493	10.933	4.1	22.2	
	Sorbitol (3%)		0.707	0.123	2.800	4.0	22.8	
	Sorbitol (14%)		21.333	3.200	57.333	2.7	17.9	

Table A.7 Literature data of water vapor permeability in films similar to starch-chitosan blend films

Material	Plasticizer	Relative Humidity %	Temperature	Water Vapor Permeability g/m.day.atm	Reference
Chitosan + Gelatin	none	N/A	Cast at 22°C	0.0061	Arvanitoyannis et al., 1998
	Glycerol (5%)			0.0963	
	Glycerol (15%)			0.3239	
	Sorbitol (4%)			0.1226	
	Sorbitol (14%)			0.3327	
	none		Cast at 60°C	0.0131	
	Glycerol (5%)			0.1138	
	Glycerol (15%)			0.4377	
	Sorbitol (4%)			0.1401	
	Sorbitol (14%)			0.5515	
Starch+Chitosan	Glycerol (25%)	0-92	Cast at 50°C	0.0343	Mathew and Abraham, 2008
Starch+Chitosan+ Ferulic acid (0.05%)				0.0309	
Starch+Chitosan+ Ferulic acid(0.075%)				0.0280	
Starch+Chitosan+ Ferulic acid (0.1%)				0.0319	
Tapioca + Chitosan(0.325% -1%)	Glycerol (0.688% - 1.25%)	n/a	Dried at 32°C Conditioned 25°C	1.304-3.064	Chillo et al., 2008

Appendix B

Experimental Data – Chitosan Content

In this section, the gas permeation data for starch-chitosan films were summarized. The data were measured under ambient temperature and 60psig.

Table B.1 Gas permeability on films with different chitosan contents without humidification

Chitosan %	Gas	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer	Selectivity O_2/N_2	CO_2/N_2	CO_2/O_2
0	N_2	1.01×10^{-6}	0.0033	0.224			
	O_2	3.59×10^{-6}	0.0016	0.582	2.6	49.0	18.9
	CO_2	6.78×10^{-5}	0.2184	10.993			
10	N_2	7.32×10^{-7}	0.0024	0.108			
	O_2	1.54×10^{-6}	0.0050	0.228	2.1	23.5	11.2
	CO_2	1.72×10^{-5}	0.0554	2.550			
14	N_2	1.05×10^{-6}	0.0034	0.112			
	O_2	2.60×10^{-6}	0.0084	0.276	2.5	19.7	8.0
	CO_2	2.07×10^{-5}	0.0669	2.207			
20	N_2	1.02×10^{-6}	0.0033	0.052			
	O_2	1.15×10^{-10}	0.0083	0.130	2.5	33.0	13.2
	CO_2	1.51×10^{-9}	0.1090	1.707			
33	N_2	4.58×10^{-7}	0.0015	0.060			
	O_2	6.58×10^{-7}	0.0021	0.086	1.4	29.2	20.3
	CO_2	1.34×10^{-5}	0.0431	1.740			
40	N_2	6.34×10^{-7}	0.0020	0.072			
	O_2	1.33×10^{-6}	0.0043	0.150	2.1	25.1	12.0
	CO_2	1.59×10^{-5}	0.0513	1.796			

(continued)

Chitosan %	Gas	Flux cm3/cm2s	Permeance GPU	Permeability Barrer	Selectivity O_2/N_2	CO_2/N_2	CO_2/O_2
50	N_2	1.15×10^{-7}	0.0004	0.015	1.7	32.3	18.6
	O_2	2.00×10^{-7}	0.0006	0.025			
	CO_2	3.73×10^{-6}	0.0000	0.473			
67	N_2	7.59×10^{-8}	0.0002	0.008	2.4	39.4	16.6
	O_2	1.80×10^{-7}	0.0006	0.020			
	CO_2	2.99×10^{-6}	0.0096	0.324			
80	N_2	2.38×10^{-7}	0.0008	0.031	2.1	29.2	13.9
	O_2	5.01×10^{-7}	0.0016	0.066			
	CO_2	6.94×10^{-6}	0.0224	0.910			
90	N_2	4.61×10^{-7}	0.0015	0.052	2.0	33.2	16.7
	O_2	9.18×10^{-7}	0.0030	0.103			
	CO_2	1.53×10^{-5}	0.0493	1.709			

Table B.2 Gas permeability on films with different chitosan contents with humidification

Chitosan %	Gas	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer	Selectivity O_2/N_2	CO_2/N_2	CO_2/O_2
10	N_2	5.53×10^{-6}	0.0178	0.351	2.2	53.4	24.2
	O_2	1.22×10^{-5}	0.0394	0.775			
	CO_2	2.95×10^{-4}	0.9524	18.731			
14	N_2	6.59×10^{-6}	0.0212	0.509	1.7	41.8	24.2
	O_2	1.14×10^{-5}	0.0366	0.879			
	CO_2	2.76×10^{-4}	0.8883	21.320			
20	N_2	7.61×10^{-6}	0.0245	0.768	1.8	43.0	24.5
	O_2	1.33×10^{-5}	0.0430	1.347			
	CO_2	3.27×10^{-4}	1.0545	33.040			

(continued)

Chitosan %	Gas	Flux cm3/cm2s	Permeance GPU	Permeability Barrer	Selectivity		
					O_2/N_2	CO_2/N_2	CO_2/O_2
33	N_2	4.79×10^{-6}	0.0155	0.932	1.6	35.4	21.5
	O_2	7.91×10^{-6}	0.0255	1.538			
	CO_2	1.70×10^{-4}	0.5471	33.009			
40	N_2	6.83×10^{-6}	0.0220	0.638	2.3	51.1	22.0
	O_2	1.58×10^{-5}	0.0511	1.481			
	CO_2	3.49×10^{-4}	1.1249	32.623			
50	N_2	4.64×10^{-6}	0.0150	0.658	2.4	55.4	23.4
	O_2	1.10×10^{-5}	0.0353	1.555			
	CO_2	2.57×10^{-4}	0.8278	36.423			
67	N_2	4.99×10^{-6}	0.0161	0.737	2.0	49.6	25.4
	O_2	9.73×10^{-6}	0.0314	1.436			
	CO_2	2.47×10^{-4}	0.7969	36.498			
80	N_2	3.03×10^{-6}	0.0098	0.538	2.8	74.4	26.3
	O_2	8.57×10^{-6}	0.0276	1.520			
	CO_2	2.26×10^{-4}	0.7275	40.014			
100	N_2	7.20×10^{-6}	0.0232	0.728	2.2	49.5	22.9
	O_2	1.56×10^{-5}	0.0503	1.575			
	CO_2	3.57×10^{-4}	1.1501	36.035			

Appendix C

Experimental Data – Cross Membrane Pressure

Appendix C summarizes the gas permeation data at different cross membrane pressures (20 to 40 psi) and chitosan contents.

Table C.1 Gas permeability with different cross membrane pressure and chitosan content

Chitosan %	Gas	Pressure psig	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
0		20	2.94×10^{-7}	0.0028	0.195
		40	6.15×10^{-7}	0.0030	0.204
	N_2	60	1.01×10^{-6}	0.0033	0.224
		80	2.01×10^{-6}	0.0049	0.244
		100	3.00×10^{-6}	0.0058	0.292
		20	1.38×10^{-6}	0.0000	0.545
		40	2.30×10^{-6}	0.0111	0.559
	O_2	60	3.59×10^{-6}	0.0116	0.582
		80	4.92×10^{-6}	0.0119	0.599
		100	6.11×10^{-6}	0.0118	0.617
		20	3.16×10^{-5}	0.3058	15.394
		40	4.87×10^{-5}	0.2355	11.852
	CO_2	60	6.78×10^{-5}	0.2184	10.993
		80	9.25×10^{-5}	0.2237	11.261
		100	1.13×10^{-4}	0.2177	10.956
20		20	2.23×10^{-6}	0.0215	0.495
		40	4.61×10^{-6}	0.0223	0.513
	N_2	60	7.16×10^{-6}	0.0231	0.531
		80	1.00×10^{-5}	0.0242	0.557
		100	1.29×10^{-5}	0.0250	0.576

(continued)

Chitosan %	Gas	Pressure psig	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
20		20	7.73×10^{-6}	0.0747	1.420
		40	1.58×10^{-5}	0.0763	1.450
	O_2	60	2.43×10^{-5}	0.0782	1.487
		80	3.28×10^{-5}	0.0792	1.505
		100	4.18×10^{-5}	0.0809	1.538
		20	1.67×10^{-4}	1.6136	37.112
		40	3.14×10^{-4}	1.5161	34.869
	CO_2	60	4.27×10^{-4}	1.3777	31.687
		80	5.40×10^{-4}	1.3067	30.054
		100	6.26×10^{-4}	1.2117	27.868
40		20	3.82×10^{-6}	0.0370	0.518
		40	7.87×10^{-6}	0.0381	0.533
	N_2	60	1.25×10^{-5}	0.0402	0.563
		80	1.69×10^{-5}	0.0408	0.571
		100	2.17×10^{-5}	0.0420	0.587
		20	1.03×10^{-5}	0.1000	1.400
		40	2.11×10^{-5}	0.1022	1.430
	O_2	60	3.26×10^{-5}	0.1052	1.472
		80	4.44×10^{-5}	0.1074	1.504
		100	5.66×10^{-5}	0.1094	1.531
		20	2.66×10^{-4}	2.5739	36.035
		40	5.03×10^{-4}	2.4315	34.041
	CO_2	60	7.09×10^{-4}	2.2860	32.004
		80	8.96×10^{-4}	2.1660	30.324
		100	1.03×10^{-3}	1.9839	27.775

(continued)

Chitosan %	Gas	Pressure psig	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
60	N_2	20	2.75×10^{-6}	0.0266	0.533
		40	5.71×10^{-6}	0.0276	0.552
		60	9.11×10^{-6}	0.0294	0.588
		80	1.26×10^{-5}	0.0304	0.609
		100	1.58×10^{-5}	0.0306	0.613
	O_2	20	7.65×10^{-6}	0.0740	1.479
		40	1.57×10^{-5}	0.0757	1.515
		60	2.39×10^{-5}	0.0769	1.539
		80	3.22×10^{-5}	0.0780	1.559
		100	3.99×10^{-5}	0.0773	1.545
	CO_2	20	1.93×10^{-4}	1.8712	37.424
		40	3.66×10^{-4}	1.7697	35.395
		60	5.10×10^{-4}	1.6455	32.909
		80	6.56×10^{-4}	1.5867	31.734
		100	7.99×10^{-4}	1.5456	30.913

(continued)

Chitosan %	Gas	Pressure psig	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
100		20	1.32×10^{-6}	0.0127	0.560
		40	3.63×10^{-6}	0.0175	0.772
	N_2	60	5.37×10^{-6}	0.0173	0.762
		80	7.98×10^{-6}	0.0193	0.849
		100	1.13×10^{-5}	0.0218	0.961
		20	2.89×10^{-6}	0.0280	1.230
		40	6.22×10^{-6}	0.0301	1.324
	O_2	60	9.74×10^{-6}	0.0314	1.381
		80	1.35×10^{-5}	0.0326	1.434
		100	1.73×10^{-5}	0.0335	1.476
		20	7.74×10^{-5}	0.7485	32.934
		40	1.54×10^{-4}	0.7455	32.800
	CO_2	60	2.36×10^{-4}	0.7617	33.513
		80	2.96×10^{-4}	0.7168	31.539
		100	3.54×10^{-4}	0.6855	30.162

Table C.2 Selectivity at different cross membrane pressures and chitosan contents

Chitosan %	Pressure psig	Selectivity		
		O_2/N_2	CO_2/N_2	CO_2/O_2
0	20	2.80	79.04	28.23
	40	2.74	58.14	21.20
	60	2.60	49.02	18.89
	80	2.45	46.08	18.80
	100	2.11	37.56	17.77
20	20	2.87	74.96	26.13
	40	2.83	67.96	24.04
	60	2.80	59.69	21.32
	80	2.70	53.92	19.97
	100	2.67	48.42	18.13
40	20	2.71	69.63	25.73
	40	2.68	63.86	23.80
	60	2.61	56.84	21.74
	80	2.63	53.12	20.17
	100	2.61	47.29	18.14
60	20	2.78	70.25	25.30
	40	2.74	64.07	23.37
	60	2.62	56.01	21.39
	80	2.56	52.14	20.35
	100	2.52	50.45	20.00
100	20	2.19	58.77	26.78
	40	1.72	42.50	24.78
	60	1.81	44.00	24.27
	80	1.69	37.16	22.00
	100	1.54	31.40	20.43

Appendix D

Experimental Data – Temperature

Appendix D summarizes the gas permeation data at different temperatures (20˚C to 40˚C) and chitosan contents.

Table D.1 Gas permeability at different temperatures and chitosan contents

Chitosan %	Gas	Temperature ˚C	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
20		20	6.53×10^{-6}	0.0210	0.610
		25	7.39×10^{-6}	0.0238	0.690
	N_2	30	8.26×10^{-6}	0.0266	0.773
		35	9.49×10^{-6}	0.0306	0.887
		40	1.03×10^{-5}	0.0331	0.961
		20	1.37×10^{-5}	0.0441	1.412
		25	1.47×10^{-5}	0.0473	1.512
	O_2	30	1.58×10^{-5}	0.0508	1.626
		35	1.67×10^{-5}	0.0537	1.720
		40	1.75×10^{-5}	0.0563	1.802
		20	2.55×10^{-4}	0.8216	27.933
		25	2.59×10^{-4}	0.8348	28.383
	CO_2	30	2.61×10^{-4}	0.8406	28.580
		35	2.79×10^{-4}	0.9003	30.609
		40	2.97×10^{-4}	0.9560	32.502
40		20	5.96×10^{-6}	0.0192	0.557
		25	6.83×10^{-6}	0.0220	0.638
	N_2	30	7.73×10^{-6}	0.0249	0.722
		35	8.44×10^{-6}	0.0272	0.789
		40	9.21×10^{-6}	0.0297	0.861

(continued)

Chitosan %	Gas	Temperature ˚C	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
40	O$_2$	20	1.49×10^{-5}	0.0480	1.391
		25	1.58×10^{-5}	0.0511	1.481
		30	1.66×10^{-5}	0.0536	1.555
		35	1.77×10^{-5}	0.0571	1.657
		40	1.85×10^{-5}	0.0596	1.728
	CO$_2$	20	3.28×10^{-4}	1.0570	30.653
		25	3.49×10^{-4}	1.1249	32.623
		30	3.57×10^{-4}	1.1501	33.352
		35	3.63×10^{-4}	1.1697	33.922
		40	3.80×10^{-4}	1.2262	35.561
50	N$_2$	20	2.73×10^{-6}	0.0124	0.422
		25	5.09×10^{-6}	0.0164	0.558
		30	6.02×10^{-6}	0.0194	0.660
		35	7.05×10^{-6}	0.0227	0.773
		40	7.38×10^{-6}	0.0238	0.809
	O$_2$	20	1.36×10^{-5}	0.0440	1.494
		25	1.42×10^{-5}	0.0459	1.560
		30	1.50×10^{-5}	0.0482	1.640
		35	1.67×10^{-5}	0.0539	1.832
		40	1.81×10^{-5}	0.0582	1.980
	CO$_2$	20	2.68×10^{-4}	0.8648	29.404
		25	2.93×10^{-4}	0.9457	32.154
		30	3.10×10^{-4}	0.9988	33.958
		35	3.15×10^{-4}	1.0156	34.532
		40	3.28×10^{-4}	1.0575	35.955

(continued)

Chitosan %	Gas	Temperature ˚C	Flux cm^3/cm^2s	Permeance GPU	Permeability Barrer
60	N$_2$	20	5.38×10^{-6}	0.0173	0.503
		25	5.53×10^{-6}	0.0178	0.517
		30	7.62×10^{-6}	0.0246	0.712
		35	8.24×10^{-6}	0.0266	0.770
		40	9.16×10^{-6}	0.0295	0.857
	O$_2$	20	1.42×10^{-5}	0.0458	1.238
		25	1.61×10^{-5}	0.0518	1.398
		30	1.77×10^{-5}	0.0570	1.538
		35	1.94×10^{-5}	0.0625	1.687
		40	2.06×10^{-5}	0.0664	1.793
	CO$_2$	20	4.15×10^{-4}	1.3389	36.150
		25	4.43×10^{-4}	1.4270	38.530
		30	4.59×10^{-4}	1.4793	39.940
		35	4.72×10^{-4}	1.5217	41.087
		40	5.00×10^{-4}	1.6116	43.512
80	N$_2$	20	3.69×10^{-6}	0.0119	0.523
		25	4.19×10^{-6}	0.0135	0.595
		30	4.85×10^{-6}	0.0156	0.688
		35	5.33×10^{-6}	0.0172	0.756
		40	6.04×10^{-6}	0.0195	0.857
	O$_2$	20	1.24×10^{-5}	0.0400	1.399
		25	1.36×10^{-5}	0.0437	1.530
		30	1.44×10^{-5}	0.0464	1.622
		35	1.54×10^{-5}	0.0498	1.742
		40	1.67×10^{-5}	0.0539	1.886

(continued)

Chitosan %	Gas	Temperature ˚C	Flux cm^3/cm^{2}s	Permeance GPU	Permeability Barrer
80	CO$_2$	20	3.19×10^{-4}	1.0269	35.943
		25	3.36×10^{-4}	1.0838	37.932
		30	3.52×10^{-4}	1.1351	39.729
		35	3.73×10^{-4}	1.2025	42.086
		40	3.92×10^{-4}	1.2627	44.194
100	N$_2$	20	5.94×10^{-6}	0.0192	0.618
		25	7.05×10^{-6}	0.0227	0.733
		30	8.06×10^{-6}	0.0260	0.838
		35	8.87×10^{-6}	0.0286	0.923
		40	9.44×10^{-6}	0.0304	0.982
	O$_2$	20	1.51×10^{-5}	0.0487	1.570
		25	1.58×10^{-5}	0.0509	1.640
		30	1.64×10^{-5}	0.0529	1.706
		35	1.73×10^{-5}	0.0559	1.804
		40	1.87×10^{-5}	0.0603	1.945
	CO$_2$	20	2.83×10^{-4}	0.9131	29.447
		25	2.92×10^{-4}	0.9403	30.325
		30	3.03×10^{-4}	0.9783	31.549
		35	3.21×10^{-4}	1.0358	33.405
		40	3.25×10^{-4}	1.0479	33.796

Table D.2 Selectivity of films at different temperatures and chitosan contents

Chitosan %	Temperature ˚C	Selectivity		
		O_2/N_2	CO_2/N_2	CO_2/O_2
20	20	2.31	45.78	19.78
	25	2.19	41.11	18.77
	30	2.10	36.99	17.58
	35	1.94	34.50	17.80
	40	1.88	33.84	18.04
40	20	2.50	55.05	22.03
	25	2.32	51.12	22.03
	30	2.15	46.17	21.45
	35	2.10	43.00	20.48
	40	2.01	41.31	20.58
50	20	3.54	69.62	19.68
	25	2.80	57.66	20.61
	30	2.48	51.43	20.71
	35	2.37	44.69	18.85
	40	2.45	44.46	18.16
60	20	2.46	71.88	29.21
	25	2.70	74.48	27.55
	30	2.16	56.08	25.97
	35	2.19	53.33	24.35
	40	2.09	50.79	24.27
80	20	2.67	68.70	25.69
	25	2.57	63.79	24.80
	30	2.36	57.73	24.49
	35	2.30	55.70	24.17
	40	2.20	51.58	23.43

(continued)

Chitosan %	Temperature ˚C	Selectivity		
		O_2/N_2	CO_2/N_2	CO_2/O_2
100	20	2.54	47.66	18.75
	25	2.24	41.38	18.49
	30	2.04	37.65	18.49
	35	1.95	36.20	18.52
	40	1.98	34.42	17.38

Appendix E

Sample Calculation

The equations used for calculation from this work are shown with sample calculations. It consists of flux, permeance, permeability and activation energy of permeation.

Flux

The flux of the gas is defined as equation E.1 and has the unit of $cm^3/cm^2.s$

$$F = \frac{Q}{S \cdot t} \frac{273.15}{(273.15 + T)}$$ (E.1)

Where Q is permeant collected from bubble flow meter (mL), S is effective area (cm^2), t is time (s) and T is temperature (˚C). The flux is normalized to standard pressure and temperature.

For example, for a film with 60wt% chitosan at 60psig and 20˚C, it took an average of 67.5s to permeate 0.5mL of CO_2. The flux of CO_2 can be calculated as

$$F = \frac{0.5}{16.6 \cdot 67.5} \frac{273.15}{273.15 + 20} = 4.15 \times 10^{-4} \frac{cm^3 (STP)}{cm^2 \cdot s}$$

Permeance

The permeance is defined as flux divided by the cross membrane pressure, as shown in equation E.2,

$$J = \frac{F}{\Delta p} \qquad \text{(E.2)}$$

where Δp is cross membrane pressure in cmHg

For the example from flux sample calculation, permeance can be calculated as the following:

$$J = \frac{4.15 \times 10^{-4}}{60 \times 5.17} = 1.34 \times 10^{-6} \frac{cm^3 (STP)}{cm^2 \cdot s \cdot cmHg} = 1.34 GPU$$

Permeability coefficient

Permeability coefficient equals permeance divided by thickness of the membrane

$$P = \frac{Q}{S \cdot t \cdot \Delta p} l = J \cdot l \qquad \text{(E.3)}$$

where l is the thickness of the membrane excluding the support. For the same example used

earlier, the permeability coefficient can be calculated:

$$P = (1.34 \times 10^{-6}) \times (0.0143 - 0.0116) = 36.2 \times 10^{-10} \frac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cmHg} = 36.2 Barrer$$

Selectivity

Selectivity of gas permeation was defined in equation 3.2 and is dimensionless:

$$\alpha_{A/B} = \frac{P_A}{P_B} \qquad \text{(3.2)}$$

where P_A is the permeability coefficient of the more permeable gas A and P_B is the

permeability coefficient of the less permeable gas B.

For the same film as in the previous example, O_2 has a permeability coefficient of 1.24 barrers. The selectivity can be calculated:

$$\alpha_{\frac{CO_2}{O_2}} = \frac{36.15}{1.24} = 29.2$$

Activation Energy of Permeation

The Arrehenius equation that describe temperature dependence of permeability is

$$P = P_o \exp(\frac{-E_P}{RT}) \tag{3.3}$$

where P is permeability coefficient, T is temperature (Kelvin), E_P is activation energy of permeation (kJ), R is gas constant, and P_o is pre-exponential factor.

Plotting P against 1/T on a semi-log scale gives a straight line with a slope of –Ep/R. For the same example mentioned earlier, the permeability coefficient of CO_2 was measured at 20 to 40°C with 5°C increment. If the permeability and 1000/T are plotted, the following figure can be obtained:

90
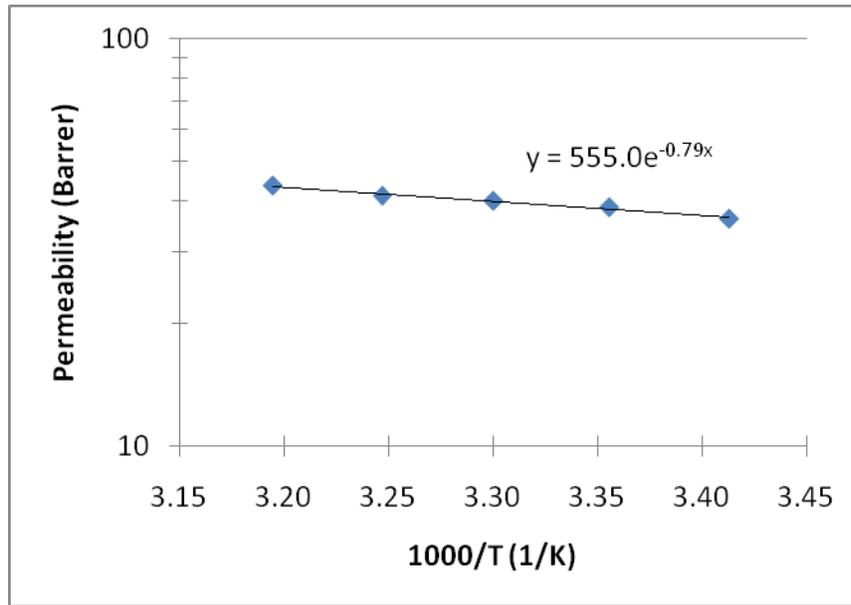
Figure E.1 Permeability versus $1000/T$ for CO_2 in a blend film with 60wt% chitosan

The best fitted line showed an equation of $y = 555e^{-0.79x}$ where

$$\frac{-E_P}{R} = -0.79$$

Therefore

$$E_P = -(-0.79) \times 8.314 = 6.57 \frac{kJ}{mol}$$

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